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LEACHING NONSULPHIDE COPPER ORES WITH SULPHUR DIOXIDE

BY

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LEACHING NONSULPHIDE COPPER ORES WITH SULPHUR DIOXIDE.

By Charles E. van Barneveld and Edmund S. Leaver.

INTRODUCTION.

In response to numerous requests from metallurgists and operators for information regarding the status of the sulphurous acid leaching undertaken by the Southwest experiment station, the Bureau of Mines issues this report, which defines the problem, states in detail the results obtained, discusses the technique of the process, and outlines plans for completing work on the problem. It is not desirable at this time to attempt to draw rigid conclusions or to discuss installation and operating costs in comparison with other processes.

ACKNOWLEDGMENTS.

The writers wish to express their full appreciation of the spirit of cooperation manifested by the officials of the copper mining companies throughout the Southwest. Special acknowledgment is made of the helpful attitude of the management of the Miami Copper Co., at Miami, Ariz., and of the Arizona Copper Co. (Ltd.), at Clifton, Ariz. The writers are particularly indebted for assistance rendered in the development of the process by Dr. H. W. Morse, consulting metallurgist, H. D. Hunt, metallurgist, and R. V. Thurston, research engineer, of the Miami Copper Co.'s staff; by Arthur Crowfoot, general mill superintendent of the Arizona Copper Co., and Kenneth Donaldson, foreman of this company's Clifton experimental mill. Acknowledgment is due to C. M. Bouton and L. E. Roberts, of the Pacific experiment station, Berkeley, Calif., for investigation of special chemical problems, and to L. R. Eckman, chemist at the Southwest station since 1919, upon whom largely devolved the chemical work in connection with the development of the process.

IMPORTANCE OF TERRITORY SERVED BY STATION.

Considered geographically, the territory served by the Southwest experiment station includes Arizona and New Mexico. Considered industrially (metallurgically), the particular mission of this station is the investigation of the field of copper metallurgy; in this field the activities of the station are not limited by the geographical boundaries stated above.

The chief metal produced in this territory is copper, although there is an important output of the other base metals, of the precious metals, and of some of the rare metals such as molybdenum and tungsten. Promising deposits of quicksilver, of vanadium, and of nickel, which are only partly developed, indicate possible future production of these metals. The coal fields of New Mexico are noteworthy, for the value of their 1918 output was nearly 11 million dollars. The combined mineral production of Arizona and New Mexico for the year 1918 is valued, in round figures, at 245 million dollars. Of this amount, 83 per cent is the value of the copper produced. In 1918 Arizona and New Mexico produced 23¼ million tons of ore, which yielded in round figures 863 million pounds of copper, a little more than 45 per cent of the entire United States output. Less than one-half of this copper (47.5 per cent) came from the high-grade smelting ores mined in the bonanza copper camps—Morenci, Bisbee, Globe, and Jerome—and at various less important localities. The remainder came from the so-called "porphyry" deposits, low-grade concentrating ores that in the main carry 1.5 to 2.5 per cent total copper which occurs as sulphide and nonsulphide copper minerals mixed in varying proportions.

HISTORICAL REVIEW.

The present era of copper mining in the Southwest had its beginning about 1800 at Santa Rita, N. Mex. (now the site of the Chino Copper Co.'s 10,000-ton open-pit mine), when Mexican operators shipped native copper from this locality to the City of Mexico, where it was coined into money. This operation was carried on until the late thirties when frequent Apache raids compelled abandonment of the mines. In the late sixties American prospectors and miners began work, and in 1873 the old Santa Rita property was reopened. In the early eighties a 40-stamp mill was built for the purpose of concentrating the low-grade native copper ores. This attempt proved unsuccessful financially because of the low tenor of the ore and the project was abandoned.

EARLY DEVELOPMENTS.

The Clifton deposits in Graham County, Ariz., first discovered by Indian punitive expeditions in 1865, were opened up by American miners in 1874. Early developments were made under great difficulties. Supplies were transported by wagon from Las Vegas, N. Mex., a distance of 600 miles. High-grade copper ores were smelted in small copper-lined furnaces of 30-ton capacity, a local development, with charcoal as fuel. The entrance of the Southern Pacific

Railway into the Territory resulted in an enlarged scale of operations, the building of a branch railroad into the district by the Arizona Copper Co., and the introduction of rectangular furnaces having a capacity of 60 to 80 tons of ore per 24-hour day, then regarded as a decided advance over the 30-ton circular furnace. At the time two companies were active in the district, the Arizona Copper Co. (Ltd.) and the Detroit Copper Co., whose joint copper production for 1883 was 5,300,000 pounds. Meanwhile, in 1879, operations had begun in the Bisbee or Warren district and in 1880 a small water-jacket furnace was erected at the Copper Queen mine. By 1883 these operations had increased so rapidly that the Copper Queen mined 34,100 tons of ore yielding 7,576,000 pounds refined copper. Similarly, in the early eighties the Globe and the Verde districts were opened and struggled along for years under the handicaps of long wagon hauls to the railroad. Coke cost $30 to $50 a ton at the smelter, and smelting costs were $12 to $16 a ton of ore.

The copper production for 1880 was considered abnormally large and the continuance of the existing demand was doubted, as is indicated by the following editorial comment by the Engineering and Mining Journal:[1]

> Demand for copper is exceedingly large, so large, in fact, that the prospect of its maintenance over long periods seems a matter subject to some reasonable doubt.

This comment is of especial interest because the world production for 1880 fell just short of 350,000,000 pounds, of which the United States furnished 60,000,000 pounds, the Arizona production being variously estimated at 3,000,000 to 5,000,000 pounds. In 1912 Arizona alone exceeded the 1880 world production and in 1918 Arizona more than doubled her 1912 production.

Another editorial comment from the same source[2] is worthy of note.

> While no one denies the existence of large quantities of high-grade copper ores in Arizona and New Mexico, we are inclined to believe that the working of lower-grade ores will, at no very distant date, attract the attention of managers and metallurgists. There are few mines which can for any great length of time keep up the strain of furnishing ores running from 15 to 25 per cent of metal to even a small smelting-plant which is capable of devouring a great deal of first-class ore. One or two concerns have during the past years shown the welcome signs of working a steadily declining average, a proof that, by greater economy, they are able to be less exacting in their sorting. The accumulation of ores, running from 6 to 10 per cent, on the dumps and in the mines, will, we hope, be an incentive to closer watching of all the details of cost. As yet, smelting raw oxidized ores for a high grade of copper with fuel generally expensive is the rule, and the metallurgical problem is one of the simplest, being reduced to the work of providing the necessary fluxing material. Soon, however, increased cost of development work, of hoisting and pumping, will counteract

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[1] Engineering and Mining Journal, Oct. 8, 1881, vol. 32, p. 234.

[2] Engineering and Mining Journal, Sept. 22, 1883, vol. 36, p. 177.

> waste, and changes in the composition of the ores will force modifications in metallurgical treatment, complicating it. In a longer or shorter time, according to locality, the engineers of that section will have to solve two questions, probably in rapid succession—how to treat their low-grade ores and how to meet the difficulties of a change in their character. It is urged, with some show of force, that, so far as the low-grade siliceous ores are concerned, especially when suitable fluxing materials can not be had and when fuel is costly, some of the wet processes of extraction would prove the most economical. Talent of the highest order and mature experience will have to be brought to bear upon the solution of these questions, which ultimately will decide the future of many enterprises.

In 1885 the London Times in the issue of August 26, under the caption "A Deluge of Copper," discusses in very pessimistic vein the outlook for copper because of the large production to be expected from the development of Montana and Arizona copper deposits. This letter drew a most interesting and prophetic reply from Dr. James Douglas.[3]

DEVELOPMENT AFTER 1885.

Concentration of copper ores in Arizona is first mentioned in 1885 in connection with jigging experiments by the Arizona Copper Co. In 1886 a concentrator was built adjoining the smelter site. The company's annual report for 1886–7 states: "The anticipations of the directors regarding the concentration plant have been fully verified." Parenthetically, attention may here be called to a most instructive discussion by Crowfoot[4] of the successive steps in the development of present concentrating practice by this company at Morenci. Mention is also made in 1887 of a concentrator at the Copper Queen mine for the treatment of copper-carbonate ores.

In 1890 the mines of Arizona produced 35 million pounds of copper from 140,000 tons of ore, the average yield per ton being 12.5 per cent. Generally speaking, 10 per cent copper ore was the lowest grade that could be handled. The introduction in 1894 of the converter at the Copper Queen smelter at Bisbee was an important forward step. The next notable advance was the introduction in 1903 of the large blast furnace at the Copper Queen smelter at Douglas, with its mechanical feeding and other improvements. As a result of better mining methods, improvements in ore dressing and metallurgical practice, and better transportation facilities, the copper industry of Arizona has expanded so rapidly that the output of ore in 1918 was over one hundred and twenty-five times that in 1890 and the copper production was nearly twenty-two times as great. Of the ore mined in 1918, 20 per cent was direct smelting ore, with an average yield of 5.2 per cent; the balance was milling and leaching ore, with an average yield of 1.25 per cent. The total copper production for the year was 765 million pounds.

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[3] Douglas, James, The copper production outlook: Eng. and Min. Jour., Oct. 17, 1885, vol. 40, p. 270.

[4] Crowfoot, Arthur, and Wittenau, Ernest, Developing a mill flow-sheet at Morenci: Eng. and Min. Jour., June 19, 1920, vol. 109, p. 1349.

ANALYSIS OF 1918 PRODUCTION.

In the following analysis of the mineral production of Arizona and New Mexico the tables given are those of the United States Geological Survey.[5] The year 1918 is chosen as being the nearest approach to a full producing year, unaffected by serious labor disturbances. The high production for the first half of the year is offset by the marked decline immediately following the cessation of hostilities in Europe.

ARIZONA.

The 764,855,874 pounds of copper produced by Arizona in 1918 came from 234 distinct producers; it is noteworthy that 88 per cent of this huge output came from 13 leading producers. The total tonnage of copper-bearing ores mined was 18,647,039 tons, of which 3,773,935 tons (roughly, 20 per cent) was direct smelting ore from which the average recovery was 104 pounds (5.2 per cent) of copper. With one notable exception the copper recovery ranged between 4 and 6 per cent. The average precious-metal recovery was $2.08 per ton, with a range of $0.50 to $4.75 by producing and smelting districts.

Mine production of metals from Arizona crude ore shipped to smelters in 1918.

BY COUNTIES.

County.	Crude ore to smelter.	Gold.	Silver.	Copper.	Lead.	Recoverable zinc.	Total value.
	Short tons.	*Fine ounces.*	*Fine ounces.*	*Pounds.*	*Pounds.*	*Pounds.*	
Cochise	1,752,728	52,420.98	2,145,406	168,450,158	2,433,494	139,878	$45,021,740
Coconino	159	.48	846	48,036	....	....	12,721
Gila	337,309	3,009.01	232,301	33,745,569	51,805	....	8,633,336
Graham	1,625	6.82	28,447	101,078	1,174,860	....	136,969
Greenlee	216,369	1,287.76	62,357	15,891,606	10,026	....	4,014,916
Maricopa	287	89.69	656	38,097	53,484	....	15,717
Mohave	3,455	965.72	39,237	435,434	578,157	82,853	215,341
Pima	258,450	45.86	128,394	17,768,821	368,172	540,027	4,593,524
Pinal	81,404	2,131.39	279,576	10,909,117	3,347,587	....	3,255,866
Santa Cruz	43,195	167.21	230,798	4,109,237	326,805	300,212	1,299,758
Yavapai	1,119,441	39,974.99	2,219,735	140,548,308	348,389	357,380	37,818,781
Yuma	30,910	1,066.36	4,752	2,337,217	97,526	....	611,013
	3,845,332	101,166.27	5,372,505	394,382,678	8,790,305	1,420,350	105,629,682

BY KINDS OF ORE.

Dry or siliceous	48,092	8,411.13	604,054	713,409	16,072	....	$955,280
Copper	3,773,935	89,854.79	4,474,440	393,336,441	3,465	....	103,486,250
Lead	19,873	2,862.53	271,476	204,473	8,463,089	....	982,035
Zinc	2,129	3.00	4,560	35,700	35,876	1,269,620	131,523
Copper-lead	916	34.82	17,578	90,374	221,259	....	56,329
Lead-zinc	387	....	397	2,281	50,544	150,730	18,265

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[5] United States Geological Survey, Mineral Resources 1918, pp. 303–306, 330–334.

Mine production of metals from Arizona concentrates in 1918.

BY COUNTIES.

County.	Ore to concentrating mills.	Concentrates produced.	Gold.	Silver.	Copper.	Lead.	Recoverable zinc.	Total value of concentrates.
	Short tons.	*Short tons.*	*Fine ounces.*	*Fine ounces.*	*Pounds.*	*Pounds.*	*Pounds.*	
Cochise	33,895	7,434	735.07	105,518	81,158	1,876,794		$274,011
Gila	7,470,382	320,490	3,644.00	244,529	173,897,683			43,272,585
Greenlee	1,836,584	229,679	2,535.00	79,789	54,204,553			13,520,716
Mohave	4,670	272	23.29	4,030	37,520	9,657		14,465
Pinal	3,555,715	259,337	5,338.00	411,108	87,689,023	507,169		22,216,652
Santa Cruz	60,937	5,497	239.80	39,626	1,257,680	1,108,284	849,293	511,204
Yavapai	159,978	42,246	7,781.34	216,516	7,891,298			2,326,522
Yuma	2,940	277	1.10	8,394		193,012		22,121
	13,125,101	865,232	20,297.60	1,109,510	325,058,915	3,694,916	849,293	82,158,276
BY KINDS OF CONCENTRATES.								
Dry or siliceous		4,379	340.32	110,829	16,372	554		$121,947
Copper		854,714	18,893.66	872,922	325,018,774			81,543,126
Lead		4,811	963.62	103,759	16,912	3,544,362		379,506
Lead-zinc		1,328	100.00	22,000	6,857	150,000	849,293	113,697

NEW MEXICO.

Of the 98,264,563 pounds of copper produced in New Mexico practically 99 per cent came from Grant County. The following table indicates the distribution of the direct-smelting ores which yielded less than 6 per cent of the copper production of the State. The remainder came from concentrating ores milled at Tyrone and Hurley in Grant County.

Mine production of metals from New Mexico crude ore shipped to smelters, 1918.

County.	Crude ore.	Gold.	Silver.	Copper.	Lead.	Zinc.
	Short tons.	*Fine ounces.*	*Fine ounces.*	*Pounds.*	*Pounds.*	*Pounds.*
Colfax	23	0.20	4	4,288		
Dona Ana	6,076	5.27	45,661	110,676	1,616,479	114,000
Grant	71,924	2,997.80	169,808	4,330,628	3,150,964	3,173,713
Lincoln	16		6	1,850		
Luna	2,910	397.35	16,442	3,150	490,493	463,445
Otero	6,270	246.52	2,142	264,417		
Sandoval	6		118	10,935		
Santa Fe	3,915	190.29	5,242	220,846	28,479	94,572
Sierra	801	27.48	18,536	42,053	25,915	
Socorro	35,024	20.80	49,835	585,482	3,033,535	7,724,087
Taos	20	2.18	149	2,162		
Torrance	637		361	78,757		
	127,622	3,887.89	308,304	5,655,244	8,345,865	11,569.817

METALLURGICAL PRACTICE AND PROBLEMS IN 1918.

CHARACTERISTICS OF COPPER DEPOSITS.

A survey of both operating practice and research in copper milling and leaching in the Southwest was made by the writers in 1917 preliminary to beginning active research work on the problem in January, 1918. The tabulation of operating and production data on milling and leaching ores for 1918 (Table 1) is substantially, if not statistically, correct.

TABLE 1.—*Operating and production data, 1918, milling and leaching ores, Arizona and New Mexico, allocated to producing companies.*

Company.	Dry tons milled.	Copper production, refined Cu, year 1918.		Copper content, per cent.								Copper recovery.					Precious metals.	
				Mill feed.				Mill tailing.					Mill recovery, per cent actual.				Gold and silver, combined value.	
		Total pounds.	Pounds per ton.	Total Cu, per cent.	Sulphide Cu, per cent.	Nonsulphide Cu, per cent.	Proportion nonsulphide to total Cu, per cent.	Total Cu, per cent.	Sulphide Cu, per cent.	Nonsulphide Cu, per cent.	Proportion nonsulphide to total Cu, per cent.	Concentrate Cu, per cent.	Total Cu, per cent.	Sulphide Cu, per cent.	Nonsulphide Cu, per cent.	Mill extraction Cu, pounds per ton.	Total in dollars.	Dollars per ton.
Milling ore:																		
Globe-Miami district—																		
Inspiration Consolidated Copper Co....	5,110,101	96,500,727	18.88	1.361	1.07	0.291	21.38	0.380	0.127	0.253	40.30	30.40	73.00	88.51	19.00	19.67	......	......
Miami Copper Co.....	2,132,941	58,407,563	27.38	2.030	1.70	.33	16.25	.590	.260	.330	55.90	40.15	71.49	85.15	1.25	28.82	......	......
Old Dominion Co.—																		
Total company and custom milling ore.....	226,998	16,095,779	70.91	3.90	......	......	......	0.49	......	......	......	......	......	......	......	70.90	151,255	0.666
Company ore.....	152,824	9,955,157	65.14	3.60	......	......	......	0.62	......	......	......	......	......	......	......	65.14	98,840	.648
Arizona Commercial Mining Co.	50,580	4,541,768	89.79	4.90	......	......	......	.47	......	......	......	......	......	......	......	89.80	31,606	.625
Iron Cap Copper Co............	23,594	1,598,854	67.76	3.74	......	......	......	.49	......	......	......	......	......	......	......	67.75	21,809	.920
Total Globe-Miami district.........	7,470,040	171,004,069	22.89	......	......	......	......	......	......	......	......	......	......	......	......	23.84	303,510	......
Clifton-Morenci district—																		
Arizona Copper Co. (Ltd.)—																		
Total both concentrators......	1,295,490	40,360,464	31.15	......	......	......	......	......	......	......	......	......	......	......	......	32.80	120,619	.093
No. 6 concentrator, Morenci....	1,128,242	......	......	2.26	1.93	.33	14.01	.73	.45	.28	79.11	13.38	71.62	79.11	28.00	......	......	......

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TABLE 1.—*Operating and production data, 1918, milling and leaching ores, Arizona and New Mexico, allocated to producing companies*—Con.

Company	Dry tons milled.	Copper production, refined Cu, year 1918.		Copper content, per cent.								Copper recovery.					Precious metals.	
				Mill feed.				Mill tailing.					Mill recovery, per cent actual.				Gold and silver, combined value.	
		Total pounds.	Pounds per ton.	Total Cu, per cent.	Sulphide Cu, per cent.	Nonsulphide Cu, per cent.	Proportion nonsulphide to total Cu, per cent.	Total Cu, per cent.	Sulphide Cu, per cent.	Nonsulphide Cu, per cent.	Proportion nonsulphide to total Cu, per cent.	Concentrate Cu, per cent.	Total Cu, per cent.	Sulphide Cu, per cent.	Nonsulphide Cu, per cent.	Mill extraction Cu, pounds per ton.	Total in dollars.	Dollars per ton.
Milling ore—Continued.																		
Globe-Miami district—Continued.																		
Phelps - Dodge Corporation, Morenci	448,884	12,174,053	27.12	1.91	......	......	......	.59	......	......	......	11.32	76.22	......	......	29.11	......	......
Shannon Copper Co.—																		
Metcalf mine	70,825	1,873,532	26.45	2.20	1.53	.67	30.05	.93	.22	.71	76.34	......	62.00	......	......	28.00	......	......
Custom milling ore	13,836	897,731	64.88	3.75	......	......	......	......	......	......	......	......	......	......	......	65.00	......	......
Total Clifton-Morenci district	1,829,025	55,305,780	30.24	......	......	......	......	......	......	......	......	......	......	......	......	31.95	120,619	......
Grant County, N. Mex.—																		
Phelps-Dodge Corporation, Tyrone, N. Mex.	585,083	15,178,760	25.94	1.928	1.651	.277	14.36	.630	.441	.189	30.00	14.875	70.232	75.72	38.00	27.15	40,991	0.070
Chino Copper Co.	3,836,400	75,655,641	19.72	1.651	1.07	.56	34.35	.647	.283	.364	56.26	14.25	63.275	75.47	40.45	20.676	39,731	.010
Total Grant County, N. Mex.	4,421,483	90,834,401	20.54	......	......	......	......	......	......	......	......	......	......	......	......	21.53	80,722	......

Pinal County, Ariz.—																		
Ray Consolidated Copper Co.	3,411,000	79,296,284	23.24	1.613	1.345	.268	16.62	.433	.220	.198	45.73	18.198	74.92	83.68	30.88	24.17	31,059	.009
Magma Copper Co.	74,000	6,364,000	86.00	4.496	......	......	......	.430	......	......	......	10.78	95.33	......	......	85.49	346,574	4.655
Total Pinal County	3,485,441	85,660,284	24.58	......	......	......	......	......	......	......	......	......	......	......	......	25.48	377,633	......
Mayer district (Yavapai County)—																		
Consolidated Arizona Smelting Co.—																		
Milling ores, company mines	104,636	4,520,370	43.20	2.57	......	......	......	.17	......	......	......	7.70	89.52	......	......	43.20	169,511	1.62
Arizona - Binghampton Co.	49,783	2,493,850	50.09	......	......	......	......	......	......	......	......	22.15	......	......	......	41.12	10,408	.29
Total Mayer district	154,419	7,014,220	45.42	......	......	......	......	......	......	......	......	......	......	......	......	42.53	179,919	......
Miscellaneous operations	53,000	1,500,000	28.30	......	......	......	......	......	......	......	......	......	......	......	......	30.00	......	......
Total milling ores	17,413,418	411,318,954	23.62	......	......	......	......	......	......	......	......	......	......	......	......	24.60	1,062,403	.06
Leaching ores:																		
New Cornelia Copper Co., Ajo, Ariz.—																		
Sulphuric acid leaching and electrolytic precipitation—																		
Electrolytic copper	......	31,222,855	......	......	......	......	......	......	......	......	......	......	......	......	......	......	......	......
Cement copper	......	10,990,666	......	......	......	......	......	......	......	......	......	......	......	......	......	......	......	......
	1,775,000	42,213,521	23.78	1.456	.051	1.406	......	.280	.060	.220	......	......	81.40	......	84.90	23.87	......	......
Shannon Copper Co., Clifton, Ariz.—																		
Sulphatizing roast and water leach; precipitation on scrap iron	24,805	264,118	10.64	.996	.45	.556	......	.51	.31	.20	......	......	51.00	......	......	10.80	......	......
Total leaching ores	1,799,805	42,477,639	23.61	......	......	......	......	......	......	......	......	......	......	......	......	......	......	......
Total milling and leaching ores	19,213,222	453,796,590	23.62	......	......	......	......	......	......	......	......	......	......	......	......	......	......	......

A glance at the milling data shows: (1) The generally low copper tenor of the mill feed; (2) an average copper extraction of 23.62 pounds refined copper per ton, with two large producers under 20 pounds per ton; (3) the practically negligible precious metal content of the milling ores, the average yield for companies producing precious metals being $0.108 per ton of ore milled; (4) the variation in the proportion of sulphide to nonsulphide copper content; (5) the effect of the nonsulphide copper on both the "total" and the "sulphide" extraction revealing the development of an economical concurrent sulphide and nonsulphide method of treatment to be the outstanding need. For the purpose of this discussion, the low-grade copper ores may be roughly classified into:

1. Clearly defined large bodies of nonsulphide ore free from sulphides or with sulphides low enough to warrant leaching the soluble copper and wasting the sulphides. Such bodies of oxidized ore are rare. Sulphuric-acid leaching followed by electrolytic precipitation of the dissolved copper is applicable to ores of this type; that the treatment is profitable when conditions warrant a large initial investment and a large operating scale is fully demonstrated by the splendid 5,000-ton leaching plant of the New Cornelia Copper Co. at Ajo.

2. Ores containing upward of 1 per cent of sulphide copper and some nonsulphide copper, from which flotation or a combination of flotation and table concentration recovers a large percentage of the sulphide copper, leaving for re-treatment a mixed tailing that contains 0.3 to 0.5 per cent nonsulphide copper. Such ores offered an immediate source of copper of which many operators took full advantage during the period of high copper prices (1915–1918). The mills were operated for maximum production of metal and were overloaded to the point of sacrificing efficiency in the recovery of sulphide copper. The mixed sulphide and nonsulphide copper in the impounded tailings constitute a retreatment problem. It was the consensus of opinion that flotation, in one form or another, would make satisfactory recoveries of *clean* sulphides that had been ground to the point of liberation. Losses in flotation plants were due partly to deliberate overloading in order to produce large quantities of copper on a high copper market, and partly to insufficient grinding. Current recoveries of sulphide copper ranged from 80 to 90 per cent. Apparently, it was merely a question of improving technique and of striking the economic balance between the increased cost of closer work and the value of the additional copper recovered.[6]

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[6] The following table, which gives the results obtained by Arthur Crowfoot and his staff at No. 6 concentrator of the Arizona Copper Co. (now a part of the Morenci branch of the Phelps Dodge Corporation), strikingly illustrates the benefit of grinding fine enough to liberate the ore particles.

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Effect of fine grinding to point of liberation of sulphides upon recovery of sulphide copper by concentration.

Fiscal year ending Sept. 30.	Mill feed.			Degree of grinding.			Recovery sulphide Cu, per cent.
	Total Cu, per cent.	Nonsulphide Cu, per cent.	Proportion nonsulphide to total Cu.	+48	+65	−200	
1917	2.44	0.36	14.75	21	30	46	80
1918	2.36	.35	14.83	21	28	48	80
1919	2.14	.32	14.95	7	16	57	83
1920	2.11	.37	17.54	4	13	63	86
1921	2.16	.45	20.83	3	12	64	88
May, 1921	2.11	.47	22.27	0	8	68	92.9

Plans for future work call for 65-mesh grinding, with 72 per cent to pass 200 mesh, in the expectation of extracting 95 per cent of the sulphide copper.

3. Mixed sulphide and nonsulphide ores differing from class 2 in that the grade of the ore is higher and that both the sulphide copper minerals and the oxidized copper minerals are present in such quantity as to make either straight leaching or straight concentration wasteful. Ores of this type, carrying around 2 per cent total copper and up to 1 per cent nonsulphide copper, frequently adjoin ores of the second type, sometimes in small patches, occasionally in large segregated bodies containing several million tons. In so far as is possible, this type of ore was and still is avoided in mining operations.

4. Accumulations of tailings from ores of the second class which offer much the same treatment problem as do ores of the third class. These tailings generally contain a considerable proportion of middling which need regrinding to liberate the sulphides. Large bodies of ore (class 3) and large accumulations of tailings (class 4) are awaiting the development of an economical concurrent sulphide and nonsulphide treatment.

5. Massive sulphide ore bodies containing a small percentage of copper in sulphide form, not enough to warrant smelting. Such ore bodies in a few localities in Arizona and in California are large enough to constitute a distinct problem.

TREATMENT OF MIXED SULPHIDE AND NONSULPHIDE ORES.

Clearly, the outstanding problem at the "porphyry copper" mines was the treatment of mixed sulphide and nonsulphide ores, and the Southwest experiment station assumed this as its major problem. Each of the companies mining these ores maintained a competent research department that experimented with concentration, flotation, leaching, and the precipitation of dissolved copper, but each had a different plan of atttack. Although the treatment of mixed sulphide and nonsulphide copper ores may be said to be a problem common to all the companies, so many variable local conditions require consideration that each company has to work out its own solution. The principal governing conditions are briefly as follows:

(1) Total amount of ore in the deposit under consideration and proportion of immediately available concentrating ore.

(2) Some mines have segregated, highly oxidized ore bodies (class 1) or have the advantage of being able to practice selective mining—for example, the Miami and the Inspiration. Other mines are not so fortunate and the entire ore body is a mixture of sulphides and nonsulphides.

(3) Mineral constituents, both copper and gangue minerals. For instance, the presence of cuprite has a decided bearing on special methods of treatment. Cuprite is only partly soluble in sulphuric acid but is wholly soluble in sulphurous acid; it is much more difficult to film or sulphidize than are the other oxidized minerals.

(4) Topography, with reference to details of transportation, water supply, tailings storage, and plant construction.

(5) Water supply and the necessity for its conservation and reuse. Settling properties of tailings from milling and leaching operations. Fouling effect of soluble constituents of different ores and its bearing on water reclamation.

(6) Smelting affiliations, local cost of leaching reagents, availability of a dependable source of sulphur.

(7) An important consideration for each company is the existing plant and the natural tendency to seek maximum utilization of the plant which usually represents a large and rather recent capital expenditure.

FLOTATION.

The uniformly high recovery of copper sulphides by flotation naturally led to flotation experiments with the nonsulphide minerals, since of all the proposed methods for complete treatment of "mixed" ores, a continuous all-flotation process was obviously the most alluring with regard to plant investment and cost of operation. It was thought at one time that sulphide flotation, followed by a filming treatment (sulphidizing) of the remaining nonsulphide minerals with Na_2S or H_2S to render them susceptible to flotation, would offer a cheap and satisfactory continuous treatment. Laboratory results were excellent and most encouraging, but results with crude ore on a 100-ton scale were most disappointing. Although no one was quite willing to declare sulphidizing and flotation to be wholly impracticable for crude ore, the expenditure of a good deal of effort and money by capable research men and operators over a period of two years had given negative results. Large-scale sulphidizing had proved a critical operation, giving widely varying results and requiring a nicety of control difficult to maintain with the class of help ordinarily available.

ROASTING AND LEACHING.

Perhaps next in promise to an all-flotation process is a roasting-leaching process. Sulphatizing roasting of crude ore, with addition of pyrite to chalcocite ores and other ores low in sulphur, at the proper temperature to convert the total copper content of the ore into water-soluble copper sulphate, sounds attractive and finds occasional persistent and devoted advocates. It seems to have received a fair trial in at least two localities. The high cost of fuel in Arizona makes the commercial success of the process doubtful even if the extraction could be made uniformly good. The main objection to the process is that the temperature must be controlled with an exactness hardly possible in large-scale operation. Whether a partial sulphatizing roast, applied so as to produce insoluble iron, followed by an acid leach, has commercial possibilities was (1918) and still is debatable. Exact regulation of temperature would not be necessary, but the roasting would have to be carried to the point of changing all the copper to an acid-soluble form and would, therefore, be costly, especially if the process had to carry the cost of grinding wet to 14 or 20 mesh and drying the pulp. Dry grinding, though a possibility, is subject to two serious objections: As usually done it is a menace to the health of workmen about the plant; grinding to 20 mesh entails the production of much flue dust. Many Arizona "mixed" ores would pay for a table treatment at 14 or even at 6 mesh preliminary to the sulphatizing roast. Most tailing ponds contain considerable material that would require grinding, and the grinding would have to be wet.

Consideration has, of course, been given to the use of a light oxidizing roast, followed by a sulphuric-acid leaching. At Anaconda, Mont., this method is successfully treating tailings—a classified sand, already dried, that presents no percolation difficulties during leaching and washing, and carries no charge for mining, crushing, or drying. To offset the low copper content of the sand and the high consumption of acid recorded, the Anaconda plant has the advantage of cheap fuel and cheap acid.

Although the recovery from Arizona mixed ores by this process would probably be high, yet the roasting plant would be expensive and the cost of the fuel might be prohibitive. The grinding necessary would be objectionable for reasons already given. Variations requiring special manipulation of the furnace or of the charge have been tried. Many combinations hitherto untried will doubtless be devised and tested in the future. Really, this would be a most enticing field for research were it not for the difficulty of reproducing on a commercial scale the results obtained on a laboratory scale by an experienced, resourceful, and dextrous investigator.

CONDITIONS IN WINTER OF 1917–18.

The situation in the winter of 1917–18 may, then, be briefly summarized as follows: Flotation of clean sulphides had been developed to high efficiency. Sulphuric-acid leaching followed by the recovery of dissolved copper by electrolysis was a demonstrated success for completely oxidized ores, though the plant investment was very high and there were many operating difficulties. The investigation of the application or adaptation of this process to mixed ores containing practically no acid-soluble gangue constituents formed part of the research program of the Inspiration Copper Co. At least three other companies contemplated extensive investigation of sulphuric-acid leaching of mixed ores and of tailings of varying composition, such as those from ores containing much limy gangue, other acid-soluble constituents that would tend to foul excessively the leaching solutions, etc. Seemingly, ample provision had been made for research in sulphuric-acid leaching and the precipitation of the dissolved copper. The outlook for a successful all-flotation process based on filming or sulphidizing the oxidized minerals was not promising, as work on a semicommercial scale had demonstrated the unreliability of laboratory scale tests and the extreme sensitiveness and delicacy of the process in semicommercial operation. Roasting-leaching had been carefully followed to the points of its elimination in one form or another as a commercial probability in this territory. There still remained the field of sulphide leaching, important more particularly for ores of class 5, massive sulphides with low copper content, since the hope of developing a sulphide copper-leaching process to compete with flotation and smelting for the sulphide content of mixed ores was very remote.

In view of the work done by the well-organized research staffs of the copper companies and the varied programs contemplated, the field seemed pretty well covered and the opportunity for independent research limited. Yet the fact remained that the problem of the "mixed" ore was still unsolved and the net results of large-scale experimental work had proved generally disappointing. What had always seemed to the writers a very promising field for research—leaching with hot sulphur dioxide gas—had been neglected.

Considerable small-scale laboratory work was done at the Southwest station to determine the behavior of SO_2 with the various ores under consideration, and the conclusion was reached that comparatively fine grinding would be necessary. All the indications pointed to a flow sheet that should include the following steps: Fine grinding to the point of liberation of sulphides; leaching with hot sulphur dioxide gas countercurrent to the pulp flow, SO_2 to be derived from the nearest available source, such as iron pyrite ores, chalcopyrite or cupriferous iron pyrite concentrates with high sulphur content; flotation of sulphides, either before leaching or after leaching; precipitation of the dissolved copper on iron, this iron to be comparatively fine sponge iron to be prepared locally by deoxidation or metallization of the iron oxide residue from the roasting operation which furnished the SO_2 gas; recovery by flotation of the precipitated copper and of any sulphide copper remaining in the pulp. It was accordingly decided to provide the Southwest experiment station with equipment for SO_2 leaching and flotation tests, the leaching range to be from hand samples to a maximum of perhaps 1 ton per hour.

SULPHUR DIOXIDE LEACHING.

HISTORY AND CHEMISTRY OF SO_2 LEACHING.

The use of SO_2 as a solvent in copper leaching is by no means new. As early as June 17, 1902, United States patent 702,582 was issued to Neill and Burfeind for leaching with SO_2 in cycle, recovering SO_2 and precipitating copper sulphite. Certain peculiarities of the chemistry of SO_2 leaching were early recognized, such as the formation of sulphites, the difficulty of retaining sulphites in solution, and the ready oxidation of unstable sulphites to stable sulphates under oxidizing conditions. Methods of treatment based on complete oxidation by air or by chemicals were proposed. In 1903 an attempt was made to utilize SO_2 at the Butters' plant, Virginia City, Nev., in a pretreatment of certain Comstock tailings, the soluble copper to be removed by use of a low-grade hot SO_2 gas before recovery of gold and silver by cyanidation. A 350-ton plant was built, following South African practice for settling and decantation. The copper was readily dissolved and oxidized to sulphate form; but through the poor settling of the slime the removal of copper solution by decantation and washing was incomplete. George C. Westby[7] refers to experimental work on smelter fumes at the Utah Consolidated Smelter in 1902-1906 which led in 1916 to the development of an SO_2 multiple-tower leaching plant at Ludwig, Nev., in which complete oxidation of copper sulphites was effected.

Sulphur dioxide dissolves rather freely in water to form sulphurous acid (H_2SO_3) which behaves like an ordinary acid except for being unstable; the SO_2 and the water are easily dissociated. The copper sulphide minerals are insoluble in sulphurous acid. In this discussion the copper minerals are divided into "sulphide copper" and "nonsulphide copper" minerals. The term "nonsulphide copper" is used to include all the minerals commonly designated in the mills of the Southwest as "oxidized", "oxide", "soluble" copper. Nonsulphide copper occurring as finely divided native or metallic copper, as cuprite, tenorite, malachite, azurite, or as chrysocolla, is completely and rapidly soluble in sulphurous acid. In certain copper silicate ores in which the copper is present as dilute, solid solutions of copper silicate in quartz, complete dissolution of the copper is sometimes decidedly slow; such ores prove somewhat refractory to sulphurous acid leaching.

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[7] Westby, George C., Sulphatizing with weak sulphurous gases, Eng. and Min. Jour., Sept. 4, 1917, vol. 104, p. 119.

Certain facts about SO_2 leaching have been pretty well established. The end reactions are simple and easily controlled. The intermediate reactions are not as yet understood. The first salt to be formed is cupric sulphite, which has several special properties. It is difficultly soluble in water, but readily soluble in H_2SO_3. It may therefore be kept in solution by maintaining a decided excess of SO_2 over the amount necessary to form the salt. When this excess of SO_2 is lost, the salt is thrown down. It has been suggested that in the old Neill and Burfeind process in which leaching was carried on with an excess of SO_2 and the exclusion of air, a bisulphite was formed:

$$CuO+H_2SO_3=CuSO_3+H_2O.$$

$$CuSO_3+H_2O+SO_2=Cu(HSO_3)_2\text{(bisulphite)}.$$

The Neill and Burfeind[8] process contemplated the retention in solution of dissolved copper in the form of copper sulphite. This can be done only in an excess of SO_2 which must be maintained not only during the leaching but during the entire decantation or filtration and subsequent washing necessary to separate clear pregnant solution from the pulp. The excess of SO_2 was removed, by steam heat or by applying a vacuum, to be reused on fresh ore, and the copper precipitated as cupro-cupric sulphite ($Cu_2SO_3CuSO_3$). Although it may seem a very simple cyclic process, many serious operating difficulties developed. The main and fatal difficulty was the inability properly to control precipitation; cupro-cupric sulphite precipitated in the pulp during the leaching, that is before decantation or filtration which is the preliminary operation in the recovery stage, causing excessive loss. Another inherent difficulty is the tendency to formation of $CuSO_4$, even in the absence of air; for any copper reduced to the cuprous state an equivalent amount of sulphurous acid is oxidized to sulphuric. This sulphuric acid seems to displace some of the remaining sulphurous acid, and hence part of the copper remains as copper sulphate, even when no air is present; the oxidation is accentuated if SO_2 can escape from the solution during heating. As a result fully 40 per cent of the dissolved copper generally was found to be $CuSO_4$, which had to be precipitated separately on metallic iron. When iron was not available, it was proposed to precipitate this sulphate copper on limestone as a basic copper carbonate, to be returned to the circuit for retreatment by SO_2.

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[8] Jennings, E. P., Leaching copper ores by sulphurous acid; Eng. and Min. Jour., Mar. 30, 1901, vol. 71, p. 400; Jennings, E. P., The Neill process at Coconino, Ariz., Eng. and Min. Jour., Jan. 18, 1908, vol. 85, p. 152; Neill, James W., The Neill process at Coconino, Ariz., Eng. and Min. Jour., Mar. 14, 1908, vol. 85, p. 556; Jennings, E. P., The Neill process at Coconino, Ariz., Eng. and Min. Jour., April 18, 1908, vol. 85, p. 821

Some rather extensive experiments were carried on during 1916–1918 by the Big Indian Copper Co.,[9] at LaSalle, Utah, under the direction of Niels C. Christensen. No details are available. In general, the experiment may be considered as an unsuccessful attempt to improve the Neill-Burfeind process.

A review of other, and later, SO_2 leaching processes reveals several combination methods in which other chemicals are added to aid SO_2 in the dissolution of copper or to prevent the precipitation of the double sulphite, or to effect the re-solution of the double sulphite after precipitation.

CHEMICAL REACTIONS.

In the method of leaching described in this paper, care is taken to supply enough oxygen, in the form of air, to insure the rapid and complete oxidation of all sulphites as they are formed; the bisulphite would not be likely to form. The main reactions to be considered are as follows:

$$\text{(Malachite) } CUCO_3CuOH_2O+2SO_2+H_2O=2CuSO_3+CO_2+2H_2O$$

$$\text{(Chrysocolla) } CuSiO_3\,2H_2O+SO_2+H_2O=CuSO_3+H_2SiO_3+2H_2O$$

$$\text{(Cuprite) } Cu_2O+2SO_2+H_2O=2CuSO_3+H_2O$$

Contact between cupric sulphite ($CuSO_3$) solutions and the mineral CuO results in the formation of both cupric sulphate ($CuSO_4$) and cupro-cupric sulphite ($Cu_2SO_3\,CuSO_3$),

$$3CuSO_3+CuO=Cu_2SO_3.CuSO_3+CuSO_4.$$

This double salt will remain dissolved in very weak sulphurous acid. When the excess SO_2 necessary to maintain sulphites in solution is expelled by aeration or by the application of heat or a vacuum, any copper in solution which has not been oxidized to sulphate will precipitate as cupro-cupric sulphite, a heavy, dark-red crystalline compound that settles readily. Once precipitated, this double salt is only slightly soluble in weak sulphurous acid, a 1 per cent solution having practically no effect. As the SO_2 content of a solution increases its solvent action increases, and in a 5 per cent solution the cupro-cupric sulphite is completely soluble.

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[9] Since this paper was submitted for publication a cooperative agreement has been concluded by the Bureau of Mines and the Big Indian Copper Co. for the installation of an SO_2 leaching plant of 200 tons capacity at the Big Indian mine. This plant is being designed at the Southwest station under the supervision of E. S. Leaver

DIFFICULTIES MET IN FORMER LEACHING WITH SO_2.

In a review of the causes underlying the difficulties met in previous work on SO_2 leaching, certain facts stand out prominently. They are summarized below.

1. It is difficult to insure sufficiently prolonged contact between the ore particles in a large mass of ore with a gaseous reagent as SO_2 or an unstable acid as H_2SO_3. The ideal procedure would be to subject the thinnest imaginable sheet of pulp of the right consistence to the action of a large excess of reagent in both the gaseous and solution form, for the time necessary to insure contact between every ore particle and the reagent, under the best possible conditions for dissolution.

2. Copper sulphites are very unstable; it is difficult to keep them in solution and to control their precipitation; moreover, they are quite easily oxidized to sulphates, and it is almost impossible to prevent some oxidation. Then why not eliminate sulphite precipitation by leaching with a large excess of SO_2 and enough air to insure prompt oxidation to the stable sulphate?

3. Sulphurous acid has one peculiar property; it is instable. The SO_2 is easily expelled by bubbling air through the SO_2 solution or by heating it; at solution temperatures above 50° C. the absorption of SO_2 is practically negligible. This instability suggested certain possibilities. The idea was conceived of utilizing in one continuous operation the solvent action of SO_2, the SO_2 expelling effect of air and heat on SO_2 solutions, and the oxidizing effect of oxygen on sulphites, thereby developing a continuous countercurrent SO_2 leaching process which would use hot roaster gas as the leaching reagent and would discharge a practically neutral pulp solution containing all the soluble copper in the form of copper sulphate.

UNSUITABILITY OF TOWER SYSTEM.

Much thought was given to the best design of apparatus for embodying this idea. A tower system was carefully considered and rejected. The following description of SO_2 leaching by a tower system is abstracted from an article by Westby,[10] which describes sulphatizing with weak sulphurous gases at the Nevada-Douglas Consolidated Copper Co. experimental plant at Ludwig, Nev., in 1916–17.

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[10] Westby, George C., Sulphatizing with weak sulphurous gases, Eng. and Min. Jour., July 21, 1917, vol. 104, p. 119.

The ore is crushed to pass a 1-inch ring and then passed over a 10-mesh screen. The oversize is treated as "coarse ore," and the undersize is separately treated as "fine ore." The coarse ore is treated as a batch charge in six closed redwood towers, each 40 feet in diameter and 21 feet high. The towers are fitted with filter bottoms consisting of spaced parallel strips, triangular in cross section, pegged to supporting stringers that rest on a foundation of 12 by 12 inch timbers brought up from the bottom of the tower. The spaces between the triangular pieces are filled with insoluble rock about egg size. There is a 4-foot space between this filter bottom and the bottom of the tower. The SO_2 gas is forced into this space by a No. 8 Sturtevant hard-lead fan through a series of oval apertures about 6 square feet in area. The coarse ore is charged into the tank dry. It is then wet down, SO_2 gas is charged through the filter bottom. Simultaneously, the top of the ore column is sprayed with leaching liquor drawn from sump tanks, which receive the drainage from these leaching towers. The drainage is effected through the filter bottom into the tank bottom proper, whence the liquor is led by a 4-inch leaden pipe to the redwood sump tanks, which are 20 feet in diameter and 8 feet high, one to each leaching tank. An outlet controlled by a valve at the bottom of the tank is connected with the inlet of a 3-inch lead pump. This pump forces the liquor from the sump tank to the spray nozzles, which are located around the inner periphery of the top rim of the leaching tower. Thus the liquors are reused as often as is necessary to build up the copper content, after which they are sent to precipitation and replaced by barren liquor and water. The unused SO_2 gas would be held in the space between the top of the ore charge and the gas-tight top of the leaching tank, whence it could be drawn and discharged into the SO_2 chamber of another tank. When the ore in a tower has been completely leached, the residue is washed by continuing a spray of barren liquor over the mass for some time. The sulphurous fumes are then diverted, the discharge doors opened, and the waste residue sluiced out. The time required for a batch treatment to effect an extraction of 95 per cent varied from 20 to 40 days continuous treatment, according to the nature of the gangue. The tonnage treated by this plant, consisting of six large tanks, six small tanks, six Sturtevant No. 8 hard-lead fans, six lead pumps for circulating solutions, and a bulky system of brick-lined iron flues for distribution of gas from furnace to tanks, was 250 tons per 24 hours.

Attempts were made to apply the same method to the treatment of fines, but it was found to be impracticable to force an appreciable quantity of gas through even limited depths of fines or through a coarse and fines mixture. Next a more reasonable method was tried. Four tanks, each 14 feet in diameter by 20 feet high, having gas-tight tops and false bottoms in the shape of inverted cones, sloping at 30° to a 7-inch discharge hole at the center, are set in line with a drop of 2 feet between successive tanks. A coned wooden latticework is built up within the tank on the periphery of the inverted false-bottom cone; this is capped by a perforated cone sloping from its apex to the sides of the tank. Each tank is equipped with a 7-inch "corrosiron" sand pump direct-connected to a 25-horsepower motor. The intake of the pump connects with the inverted cone-tank discharge. A 6-inch discharge pipe rises vertically to the top of the tank and enters a square wooden conduit, direct-connected with an elbow which is flanged to the rim of central opening in the top of the closed tank, situated immediately above the perforated cone. These wooden conduits for the four tanks are interconnected. The operation is quite simple. The mixture of fines and liquor falls in retarded cascades over the slatted cone against rising SO_2 gas. This partly leached pulp discharges through the central opening into the pump intake and is returned to the cone. As the mixture flows through the wooden conduit box, it is bled by a movable deflection plate, and the deflected portion is charged to the next lower tank in the series, the lowest tank discharging to the washing and clarifying system. On the basis of 50 tons per 24 hours, the extraction on various tests ranged from 60 to 90 per cent. It was estimated that a battery of nine tanks in series, each 14 by 30 feet and equipped with 8-inch sand pumps, would be required to effect a 90 per cent extraction on 250 tons daily.

A serious objection to this method is the rapid erosion of the working parts of the sand pumps. In order to eliminate this objection experiments were made with towers of varying construction which would not require any pumping of sand. The internal arrangement of the tower comprises a latticework of superimposed staggered shelves built from the foundation up. These shelves are built of three or more 1 by 1 inch strips set sufficiently close to prevent damp or wetted fines from falling freely through the slits so formed, yet not close enough to prevent percolation from the ore heap on the shelf or to prevent the freest introduction of vapors to the bottom of the ore heap. The space between parallel superimposed shelves is 3 inches, the space between shelves in the same layer varies between 1 and 2 inches. The tower is charged with fines from the top. The charge progressively falls from shelf to shelf throughout the tower as the upper layers of shelves become heaped up and the excess material drops onto the shelves below. The tower is thus gradually filled with little heaps or piles of ore, small enough to admit of penetration of reagent to the center of the heap. When the tower is filled sulphurous vapors are admitted through a flue entering the base of the tower. A steam jet is used to supply the water vapor necessary to moisten the entire pulp charge and to insure proper propulsion and distribution of the SO_2 gas. The combination of hot gas and steam decidedly accelerates the necessary chemical reactions. When the charge has been thoroughly sulphatized the simplest final treatment would seem to be to obtain clear solution by sluicing out the charge into a Dorr classifier. If it is necessary to guard against dilution of copper solution, this sluicing could be done by using slimy liquor from the classifier until the

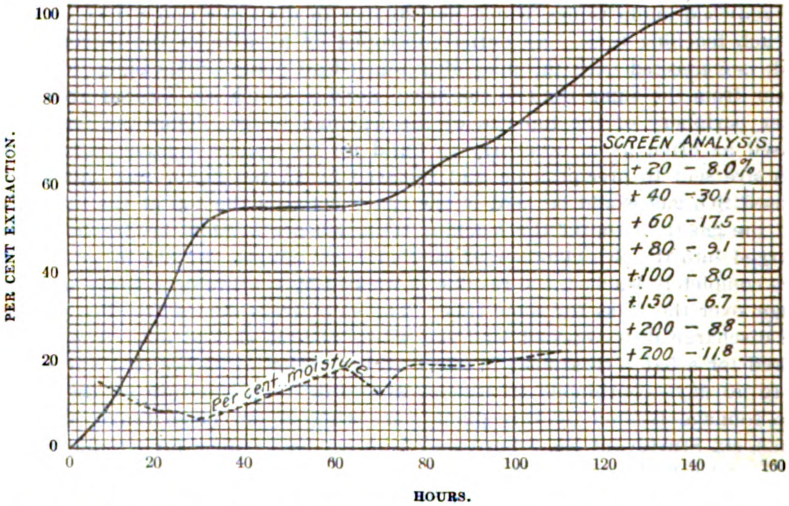


FIGURE 1.—Curve showing results obtained by shelf-tower treatment of 10-mesh ore at Nevada-Douglas plant.

tower is cleaned. The curve, Figure 1, indicates results obtained by treating 10-mesh ore with 1.2 per cent SO_2 fumes by the shelf-tower method, 90 per cent dissolution resulting in 120 hours' treatment.

This abstract of Nevada-Douglas operations is included here because the present writers visited the Ludwig plant and observed its operation in the winter of 1917. They were impressed with the value of this demonstration of sulphatizing leaching with weak sulphurous gas; moreover, they were particularly impressed with the necessity for replacing the tower system by apparatus more efficient and more easily controlled.

MECHANICAL MEANS FOR DISSOLUTION AND OXIDATION.

A study of possible mechanical means of effecting the intimate mixture necessary for rapid and complete dissolution and oxidation of copper showed that a cell similar to the rapid agitation type of flotation machine, in which the revolving mechanical agitation is so rapid as to literally beat the gas into the pulp, would do the work. The objection to this class of apparatus is that it requires nonmetal, acid-proof construction. The pneumatic type of flotation cell also would give satisfactory admixture and contact of pulp and reagent, provided practical details of use could be satisfactorily worked out. The regular cotton blanket is quickly destroyed by SO_2. All-wool blankets, however, endure. Bottoms made of "filtros" or of cemented sand quickly clog; bottoms made of Monel metal do not give the requisite fine division of air; only the all-wool blanket seems satisfactory in this respect. Under the best experimental operating conditions it did not seem possible to obtain over 6 per cent utilization of SO_2 in a single pass of gas through the cell, therefore tight-top cells built in series would be necessary. With such construction the necessary raking of the porous bottoms—all forms of porous bottoms need constant attention to keep them open—would be difficult. After diligent inquiry, no compressor has been found that will satisfactorily handle hot moist SO_2 gas. No form of design occurred to the writer. Under the circumstances this line of research was abandoned, and attention was centered on the design of a continuously revolving drum which had been in mind since the problem was first considered.

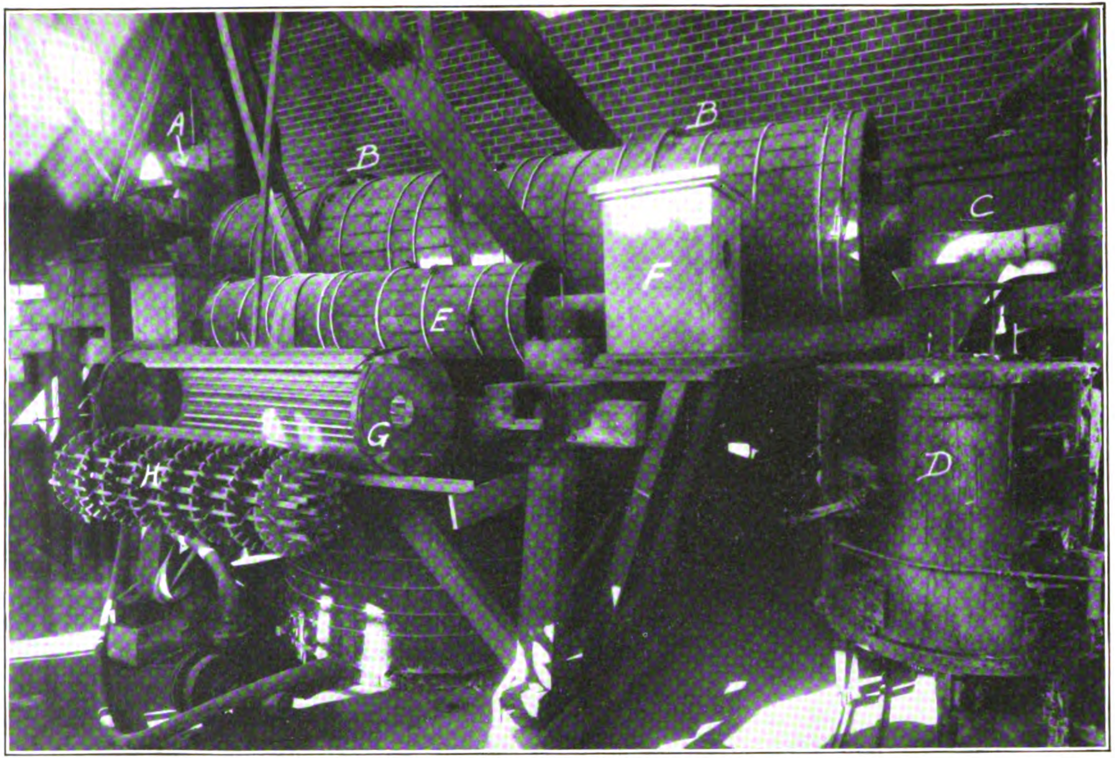
TUCSON EXPERIMENTAL PLANT.

APPARATUS.

The apparatus as finally designed and constructed in January, 1919, at the laboratories of the Southwest experiment station is shown in Plate I. It consists of a pulping tank, *A;* a horizontal drum, *BB;* and a specially designed Herreschoff roasting furnace, *D*. The two small drums *E* and *G* are recent additions. The drum *G* is shown in course of construction with the interior baffle arrangement *H* removed and suspended in the foreground. The drum, 4 feet in diameter and 16 feet long, inside dimensions, is made of wooden staves and is set to rotate slowly on a horizontal axis; it is belt driven and rests on a pair of flanged trunnions. These trunnions are hidden from view by the drum *E* and its pulp discharge box *F*, but are immediately under the tires at *BB*. The inner periphery of the drum is provided with lifters, on the plan of a South African tailing wheel, which act as elevator buckets and in their ascent, as the drum rotates, they pick up the pulp and finally spill it onto a series of staggered horizontal 2 by 4 inch baffles, so placed that the pulp is splashed and distributed over their surfaces in fine drops and particles. The length of the drum is divided into 12-inch compartments by a series of transverse partitions, hereafter termed vertical disk baffles. The longitudinal baffles extend the full length of the drum, and the openings for them in the vertical baffles are enlarged to give immediately above each longitudinal baffle a semicircular opening through which the pulp and the gases travel countercurrent to each other. These holes are faintly discernible at *H*, Plate I, and show clearly in Plate III.

OPERATION.

The ore, ground to 30-mesh or finer, is pulped in the tank *A* to the proper consistency (the ratio of water to ore may vary from 1:1 to 4:1) and is fed into the drum where it drops to the bottom of the first compartment. The drum rotates slowly, the lifters pick up their load and elevate it. The longitudinal baffles are so situated as to cause the greatest possible splashing of the pulp when the lifters begin to spill. The pulp is thus splashed and distributed over the horizontal bars and against the vertical disk baffles, in fine descending drops and particles; thus intimate and prolonged contact between the pulp and the countercurrent sulphurous and oxidizing gases is assured. Under the influence of a constant feed of pulp the flow is established within the drum, and the pulp gradually passes through the successive compartments into the last or discharge compartment. In this compartment the lifters raise the pulp and drop it into a discharge or exit pipe whereby it passes through a trap (*C*, Pl. I) opening into the discharge launder. Some of the pulp spilled from the ascending lifters finds its way through the holes in the vertical disk baffles into the next compartment, is lifted to the top of this compartment and subjected to the same showering action, and so on through each compartment to the point of exit.



TUCSON EXPERIMENTAL SO_2 LEACHING PLANT.

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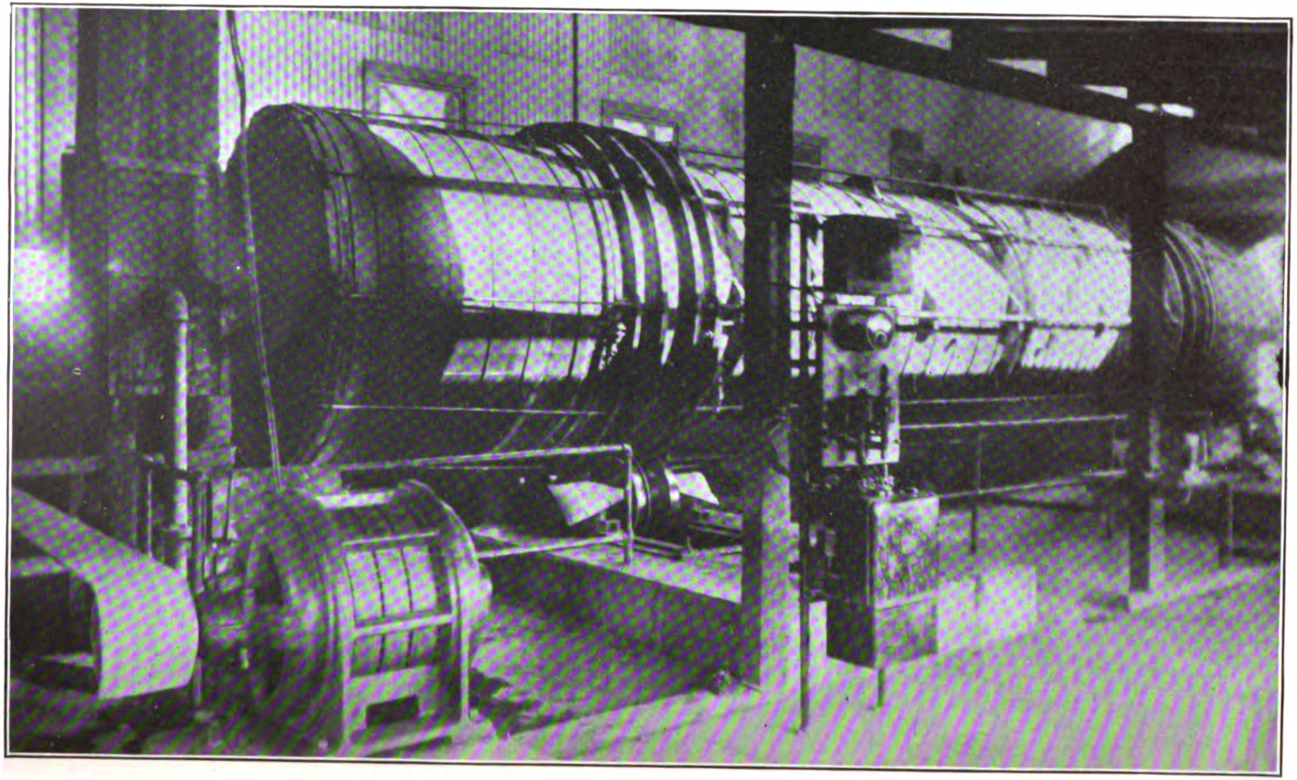

MIAMI 100-TON SO_2 LEACHING DRUM.

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The pulp enters one end, *A*, of the drum cold. The reagent, heated combustion gases from the roaster *D*, usually contains less than four per cent SO_2 by volume for ordinary ores and a higher percentage for ores containing acid-soluble gangue minerals; it enters through the top of the trap box *C*, which is also the pulp discharge box. By the countercurrent flow the pulp becomes progressively warmer and the gas correspondingly cooler until the pulp at the discharge end is heated to any desired temperature. At a temperature of 50° C, the absorption of SO_2 is practically negligible. The hot pulp discharged from the drum at this temperature contains practically no free SO_2 and may be considered neutral. As the temperature decreases, the absorption of SO_2 throughout the drum progressively increases.

REQUIREMENTS FOR GOOD OPERATING CONDITIONS.

The requirements for good operating conditions of the drum may be summarized as follows: Enough SO_2 must be introduced to effect rapid dissolution and enough oxygen must be present to effect rapid oxidation of sulphites to sulphates. Enough sulphur (in whatever form) must be burned to heat the gas to the point that will produce the desired terminal pulp temperatures. The density of the pulp will be one limiting factor in the capacity of the drum, because for any given temperature and volume of furnace gas the discharge temperature of the pulp will vary inversely as the volume of solution the gas must heat. Thus for each particular case there is a proper relation between pulp density, admission temperature of gas, dilution of gas, and leaching efficiency, which will determine the quantity of sulphur (pyrite) to be burned. Approximations may readily be made in each case from a knowledge of the conditions; subsequent regulation of the variable conditions is a simple matter; from this the requirements may be accurately determined and positively maintained. It may be assumed that a greater dilution than 1½ parts of water to 1 part of ore will rarely be necessary to obtain the proper conditions for rapid dissolution, and a 1 to 1 pulp will frequently be found satisfactory.

FIRST TRIAL OF PLANT.

The first trial of this plant was made on what seemed the most readily available material, namely, oxidized mill tailings remaining from former operations of the Detroit Copper Co., the Arizona Copper Co., and the Shannon Copper Co. in the Clifton-Morenci district. A carload of tailings comprising six or seven lots, was shipped jointly to Tucson by these three companies. The tailings carried 1 to 1.25 per cent total copper and 0.48 to 0.75 per cent nonsulphide copper. Results of leaching were very satisfactory. The sol-

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uble copper in the tailings after treatment was maintained at 0.06 per cent; the drum did not develop any operating difficulties and its capacity was considerably larger than the original estimate. Dr. H. W. Morse, then acting as consulting metallurgist for the Miami Copper Co., became interested in the possibility of SO_2 leaching of Miami ores and arranged for a shipment of mixed ore, high in oxidized copper, which had been put through the regular sulphide flotation; the tailings were then drained, dried, and sacked for shipment. The feed assayed 0.80 per cent total copper and 0.59 per cent nonsulphide copper. On a 2,500-pound run the nonsulphide leaching-drum tailing, because of a low density pulp leach (3:1), contained an average of 0.06 per cent copper. On a similar run at high pulp density (3/4:1) the average nonsulphide copper content of the leaching drum tailing was 0.13 per cent. As a result of these confirmatory tests a cooperative agreement was made by the Bureau of Mines and the Miami Copper Co. whereby the latter agreed to erect a 100-ton leaching unit with all the supplementary equipment necessary to produce copper on a 100-ton scale.

MIAMI 100-TON SO_2 LEACHING PLANT.

Preparations for construction of the Miami plant were well under way before the World War dislocated the entire business of the country. Construction was necessarily slow. The main consideration of the Miami Copper Co. was, of course, to maintain copper production during a period of high prices, when operation was complicated by transportation difficulties, labor troubles, scarcity of men and supplies. The plant was first put in operation in February, 1919. Many imperfections in construction were due to the enforced use of material already on hand. For instance, the inside diameter of the drum was fixed by the fact that some old Hardinge mill castings, 8 feet inside diameter and 18 inches wide, were available as carrying supports for the drum. It seemed better to use these than to risk delays in the delivery of proper tires. The intention was to use 6-inch staves for the drum proper, but only 3-inch redwood lumber was available and the resulting inside diameter of the drum was 7 feet 4 inches. Calculations based on the performance of the Tucson 4 by 16 foot drum indicated that the Miami drum need not be over 30 feet long to give 100-ton capacity; 10 feet was added as a factor of safety and the new drum was designed with 40-foot inside length.

CONSTRUCTION OF DRUM.

Details of interior construction are plainly indicated on Plate III. The elevator lifters are made of common 1¼ by 5 inch rough lumber set at 30° in a groove cut in the staves. These lifters are fastened with plain wooden pins. The vertical disk baffles are made solid of 2-inch lumber set at 12-inch centers along the drum. Under each of the tires, which are wedged to the outside of the drum, the disk baffles are doubled, giving a 4-inch support at these points in case of flexure of the staves. This 12-inch spacing of disk baffles gives large absorption surface and still leaves enough space between baffles to insure proper distribution of gas in the compartments; it also leaves enough space to permit inspection and repairs.

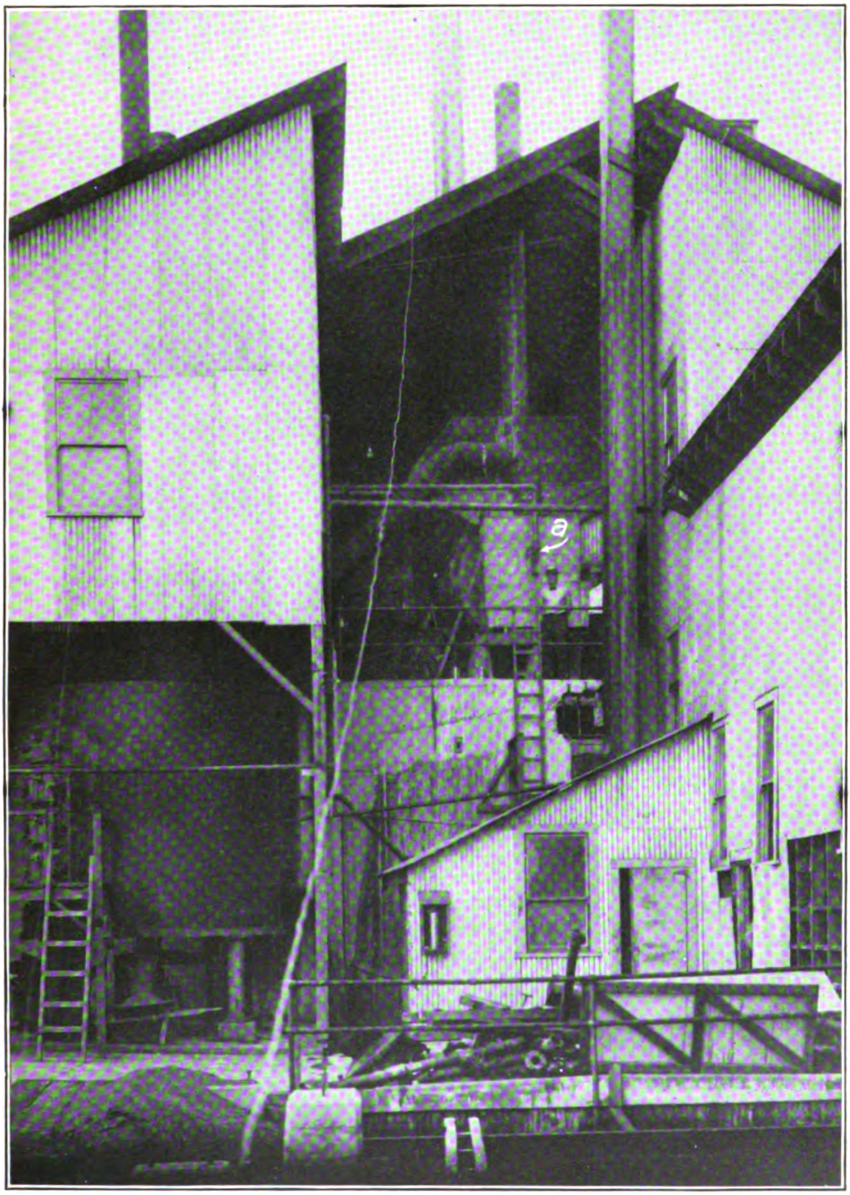
In order that workmen may have access to the drum at any point, a squirrel cage or manway is provided (Pl. III). In cross section the wall of this squirrel cage consists of alternating 2 by 4 inch staves and 2 by 4 inch openings, set in a circle of 24-inch inside diameter. This ring of longitudinal baffles is securely pinned with wooden dowel-pins to the inner rim of the vertical disk. The main vertical disk baffles have central circular openings 28 inches in diameter. At every third vertical disk these blank spaces in the squirrel-cage wall are blocked with solid blocks, 3 inches long, fastened to the inner rim of the disk with wooden dowel pins. To prevent the gas from rushing along the axis of the drum, this passageway is plugged at regular intervals and divided into a number of central sections along its length by solid removable disk partitions placed at any of these "blocked" vertical disks and completely closing the passageway. These plugs may thus be placed at 3-foot or 6-foot or 9-foot intervals. The gas can only enter and leave the central sections through the open spaces in the squirrel-cage walls. The drum may be entered and inspected at any point and may be repaired by removing first the solid plugs, next the necessary small plugs, and finally as many of the longitudinal baffles forming the squirrel-cage wall as may be necessary. This is not a difficult or lengthy job. Besides maintaining a passageway, the squirrel-cage baffles serve as regular splash baffles.

At first the drum at Miami gave considerable trouble. The flanges on each side of the old ball-mill castings formed the tire surface, and revolved on 12-inch car wheels. A sprocket drive fitted around the center of one of the 8-foot castings turned the drum. This arrangement was far too light; it gave endless trouble and was a continual source of delay and expense. Finally, the trouble was remedied by placing over the circumference of each casting two tires made of 90-pound rail, turned to a circle and properly held in place by set screws (see Pl. II). These new tires were supported and revolved on standard 30-inch railroad-car wheels, two pairs on opposite sides of the drum at each end, eight in all. On one side of the drum each set of wheels was pressed on a separate 4-inch steel shaft supported by end bearings. On the opposite side a continuous shaft, which formed the friction trunnion drive, carried both sets of wheels. The drum is driven by the trunnion shaft mentioned above. Details of this drive are not shown in any of the drawings; it stood up satisfactorily. The 3-inch redwood-drum staves proved too light and had to be reenforced. After the drum had rotated for a while, the staves were found to "creep." This trouble was remedied by driving home double-tapered wedges at each side, between the track supporting castings and the outer face of the drum stave until all movement was taken up. After a few days all tendency to creeping of the staves stopped.

The terminal details of the drum are shown in Plate III. At the cold end of the drum (right-hand) is a square wooden gas stack, made of 2-inch plank, designed to carry off the spent gas. The pulp enters through a 4-inch pipe near the bottom of this stack and flows into the drum through the sleeve made of 20-inch wood-lined pipe. One of the important construction details is the gas seal, at either end of the drum; it must prevent leakage of gas and yet permit both vertical and lateral movement. The tire seal shown serves very well for the cold end, but did not serve at the hot gas intake end and was replaced in the Miami drum by a movable pedestal joint. (See Pl. IV.) Plate III does not show this seal but an improved design, submitted by the Allis-Chalmers Manufacturing Co. The seal is bolted to the wall of the concrete discharge trap. The pulp flows through the trap and the gas is admitted through the large pipe that enters at the top. This block rests on a track supported by a solid concrete foundation; it may be moved back enough to give access to the interior of the drum from that end.

ARRANGEMENT AT PLANT.

The arrangement at the Miami 100-ton SO_2 leaching unit is best described verbally. The ore, already crushed to $\frac{1}{2}$ inch, is delivered to the plant in lots of 350 tons, and is fed by a mechanical revolving disk feeder to a Hardinge mill operated in circuit with a Dorr classifier set to deliver a maximum of 1 per cent on 48-mesh. By means of a cut-out set between the ore bin and the ball mill the tonnage delivered to the mill may be determined accurately. The entire flow of dry ore is intercepted and deflected for any desired period. The weight of this sample and the time factor give the necessary data for accurately calculating the tonnage. The feed to the ball mill is preoiled and the pulp is discharged at a density of $3\frac{1}{2}:1$ to $4:1$ to a pneumatic flotation unit consisting of four roughing cells and one cleaner cell. The flotation tailing is thickened to a density varying from $1\frac{1}{2}:1$ to $1:1$, and fed to the leaching drum, where it is leached by hot SO_2 gas direct from a 10-foot Herreschoff roasting furnace. The entire flow of the leached pulp is conveyed by a tight



ROASTING FURNACE AND GAS-INTAKE END OF MIAMI SO_2 LEACHING PLANT.
a, GAS-SEAL PEDESTAL JOINT.

launder to a 3-foot by 20-foot iron precipitating drum, lined with wooden blocks set in acid-proof cement, which is run at 4 revolutions per minute. The regular charge consists of 10 tons of 2-inch steel balls, which wear down smoothly until they are consumed; balls are added daily to keep the weight constant. The iron consumption is 1.2 pounds of iron per pound of Cu precipitated. The fineness of the cement copper ranges from 200 to 1,000 mesh. The overflow from the thickening before leaching rejoins the thick pulp discharged from the precipitation drum and restores the pulp to the proper density for the second flotation, which is performed in a flotation unit similar to the upper unit.

SO_2 SUPPLY.

A 10-foot, 6-hearth Herreshoff roasting furnace, requiring two motors of 2 indicated horsepower each, supplies the SO_2; it can supply enough SO_2 for a 250-ton plant treating this ore. That it gave very satisfactory results when operated at reduced speed is indicated by the fact that 2.5 tons of massive pyrite containing 44 per cent iron and 50 per cent sulphur was regularly roasted down to less than 2 per cent sulphur. The calcines contained around 60 per cent iron, 10 per cent insoluble matter, 1.8 per cent sulphur, and 0.5 per cent copper, an unusually fine product for further deoxidation treatment for the production of sponge iron. A No. 8 Buffalo blower, run by a 5 indicated horsepower motor, is used to convey the gas from the roasting furnace to the drum intake, and the volume of gas passing is controlled by regulating the blower speed.

At this point mention should be made of a source of danger, in fact, the only serious source of danger to the entire operation. A cut-out must be provided in the gas intake to divert the hot gas to the smokestack and to prevent the hot gas from entering the fan and the drum when the latter is not running. So long as wet pulp is discharging at the gas intake there is no danger from fire. When the drum is idle the woodwork is soon dried to the point where a hot gas will ignite the wood. During the early operation of the Miami drum a trunnion axle broke. The fan was stopped, as were the furnace rabble arms. The shiftman did not realize that the natural draft from the drum exhaust stack would be sufficient to continue the roasting action in the furnace. In about four hours the interior of the drum was on fire. It burned rapidly, and one-third of the interior woodwork was destroyed before the fire could be extinguished. A positive gas cut-out was then inserted between the furnace and the fan to eliminate the danger.

POWER REQUIREMENTS.

The power requirements for the plant are light—less than 20 actual horsepower. The leaching drum is rotated by a 25 indicated horsepower motor, actual power consumption 12 horsepower. The motor for the blower and the two motors for the roasting furnace have a combined rating of 9 indicated horsepower.

DETAILS OF OPERATION.

The plant began operation in February, 1919, on a 2 per cent ore carrying about 1 per cent nonsulphide copper. The early results gave an 81.7 per cent dissolution of nonsulphide copper and a tailing that averaged 0.17 per cent. Precipitation of the dissolved copper was complete, but no precipitated copper was recovered by flotation. The reason for this was soon discovered. The precipitating drum discharge carried much free SO_2 and unoxidized sulphites, principally iron sulphites. The temperature of the pulp as it left the drum was only 28° C., whereas the best work at Tucson was done at an exit temperature approximating 50° C. To correct this condition the suction fan and all the pipes from furnace to drum were covered and the motor pulley driving the fan was enlarged. This resulted in increasing the volume of gas and raising the temperature. Soon the solution temperatures were up and some cement copper was floated. During a short furnace repair the temperature of the solution dropped from 40° C. to 28° C., and flotation was lost. It was evident that free SO_2 or sulphites in the pulp prevented flotation of cement copper.

In order to insure complete oxidation and freedom from SO_2, two flotation cell bottoms were placed to receive and aerate the pulp from the leaching drum, the pulp flowing over them in a thin stream. Air under 4-pound pressure, entering through the blanket bottom, kept the pulp agitated and expelled the free SO_2. On account of corrosion, these cells were replaced by two and later by three wooden tanks, 4 feet square, 6 feet deep, set in series, in which the pulp was aerated by an air jet through the bottom. The pulp entered at the bottom, overflowed at the top, and the period of aeration was about 30 minutes. This installation was a rather crude makeshift; it could, of course, be improved. An acid-proofed flotation cell with woolen blanket bottom is the more efficient arrangement. During this time the drum was taking the regular tailing discharge from the sulphide flotation plant at 4:1 density. Then the thickening tank was added and pulp of 1:1 density was delivered to the drum. With this thickened pulp flowing countercurrent to a 2 per cent SO_2 gas, and with proper insulation of pipes, the discharge solution temperature was easily maintained at 40° to 48° C. The pulp as discharged contained around 0.2 per cent total sulphites; this was reduced to 0.01 per cent by passing through the blower cells. Copper precipitation was complete. To all appearances flotation conditions in the first cell were good, a color of copper was noted on the second and third cell, and only a white froth on the fourth cell. Apparently, good operating conditions had been attained, and for several days the flotation of cement copper was fairly good.

The arrangement of the plant made maintenance of this good balance impossible. The thickened pulp which constituted the drum feed was obtained in the following manner: The ball-mill discharge was fed to a cone classifier, the overflow from which was fed to a Dorr tank designed for thickening slimes. The classified sands and thickened slimes were drawn through variable size spigot openings, generally maintained at ½ inch diameter, in the tank bottoms. The combined products of these two tanks constituted the drum feed. Wooden chips often clogged the openings, retarding or stopping the flow. In cleaning out these discharge plugs, the pulp would often "break through" in large volume, sending a large excess of feed to the drum. The suddenness of this fluctuation in feed and its relatively large range had much to do with upsetting the plant balance, the bad effect being most noticeable in the flotation of cement copper. This happened many times during each shift.

PLANT CONTROL.

The process is easily controlled, it has no critical points, and no fine adjustments are required. Ordinarily intelligent supervision and attention to half a dozen simple details are needed. Proper crushing and regularity of feed are important; reasonable variation in feed is permissible. Gas volume, SO_2 content and temperature are easily controlled. At the Miami plant SO_2 content and temperature of gas at entry and at discharge of drum were recorded twice on each eight-hour shift. The temperature of the entering gas was maintained as nearly as possible at 240° C. The exit temperature usually coincided with the temperature of the entering pulp—about 26° C. The SO_2 content was maintained at 2 per cent by volume and a 60 per cent absorption within the drum was obtained. Raising or lowering the SO_2 content of the gas did not in itself affect the rate or degree of dissolution, the essential condition being the constant maintenance in the drum of a slight excess of SO_2 over the requirements of the acid-consuming constituents of the ore. The temperature of the discharged pulp was recorded at 30-minute intervals; it affords a quick method of detecting changes in furnace product or in reactions within the drum. The pulp was tested at intervals of one hour for SO_2, both at the exit from the drum and after passing the blower tanks.

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PULP DENSITY.

Pulp density was tested every hour, and oftener when fluctuations in results indicated disturbance in the thickeners which controlled the quantity and condition of feed to the drum. Samples were taken in the following manner: An ordinary wide-mouth bottle was chosen of such size that when filled with 500 grams of wet pulp the 500-gram mark reached into the neck of the bottle. A 500-gram sample was taken by cutting the pulp stream with this bottle. The net weight of the pulp sample was obtained and by comparison with a prepared chart the "solution to ore" ratio was read at a glance. Charts may readily be prepared for any conditions or requirements by use of the following formula:

$$P = \frac{100S\,(a-l)}{a\,(S-l)}$$

$$\text{Ratio} = \frac{100-P}{P}$$

in which P=percentage of dry slime in wet pulp;
S=specific gravity of dry slime;
a=specific gravity of wet pulp; and
l=specific gravity of solution.

This formula is accurate enough for this work. It will be noticed that the specific gravity of the solution is given as l; on account of the solubles carried in solution the specific gravity would increase. Should a correction for this be desirable, use the following formula:

$$P = \frac{100S\,(a-d)}{a\,(S-d)}$$

in which a=specific gravity of wet pulp;
S=specific gravity of dry slime;
d=specific gravity of solution; and
P=percentage of dry slime in wet pulp.

Anyone desiring complete information on this subject is referred to an exhaustive treatment of the subject by Clevenger.[11]

SAMPLING AND ANALYTICAL CONTROL.

The analytical control of the process is quite simple. Seven determinations are required, descriptions of which will be found on pages 73–81.

SAMPLING.

The importance of proper sampling is obvious. Noncorroding vessels must be used, such as fiber buckets, stone crocks, glass bottles.

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[11] Clevenger, G. H., Young, H. W., and Turner, T. N., Pulp constants, Eng. and Min. Jour., Dec. 19, 1914, vol. 98, p. 1075.

Enamel ware must not be used under any conditions, as the very best enamel is not proof against copper solutions. If an enamel bucket is allowed to stand overnight filled with discharge pulp from the drums, and this pulp is carefully poured off, the sides of the bucket will be found covered with fine hairlines of precipitated copper. The solutions discharged from the leaching drum are practically neutral. Therefore it is necessary in preparing samples for assay by decantation and washing to keep the wash water very slightly acid. Careless washing with ordinary alkaline water, with resulting dilution of pregnant solution, will cause precipitation of considerable dissolved copper as hydroxide or as carbonate, which would salt the tailings and be reported as unleached soluble copper.

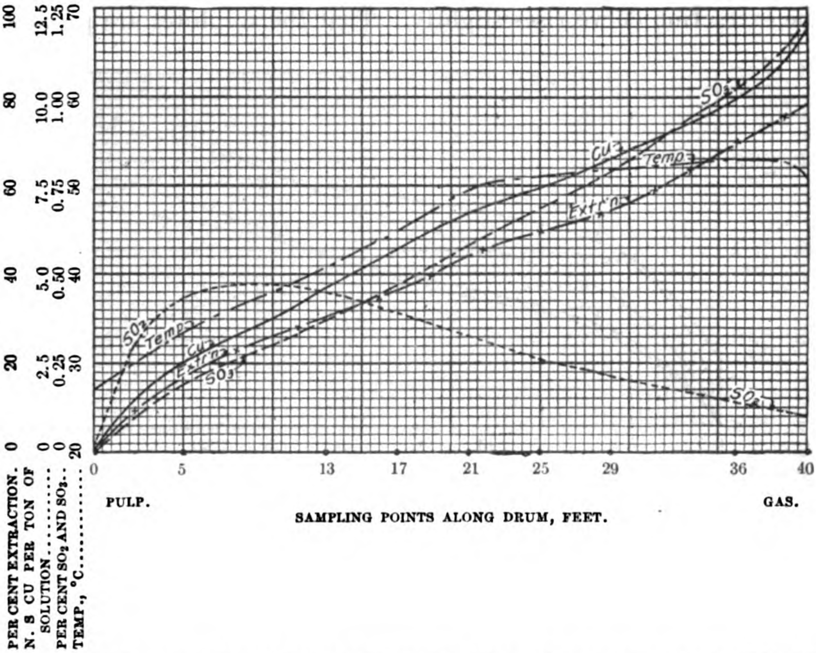

FIGURE 2.—Test A, April 28, 1919. Entering gas, SO_2, 1.48 per cent; exit gas, SO_2, 0.58 per cent; copper (n. s.) feed, 1.15 per cent; pulp density, 1.44; tails, 0.25 per cent; leaching extraction, 78.3 per cent.

SUMMARY OF MIAMI LEACHING RESULTS.

Table No. 2 (p. 34) presents a comparative summary of average monthly leaching extractions over a period of 11 months. The results for February, 1919, were fair, everything considered. The results for March and April, however, were bad, and the extraction was plainly much lower than that obtained at Tucson. It was desirable to sample the pulp in the drum at sufficiently close intervals to permit study of the progressive changes. A series of 2-inch holes was bored at 4-foot intervals along the drum. The four charts presented in Figures 2, 3, 4, and 5 are fairly representative of the variable leaching conditions. The results are consistent. The copper extraction curve rises sharply for the first 5 to 10 feet indicating dissolution of the easily soluble carbonates. Thereafter the rise is more gradual as the higher silicates are dissolved. Finally the curve becomes flatter as the more resistant solid solutions of copper silicates are partly leached. Toward the end of the drum where the heat is greatest the extraction curve rises slightly. That the sulphites are promptly oxidized to sulphates is indicated by the general parallelism of the SO_3 curve and the extraction curve. The SO_2 curve indicates a rapid absorption in the first 10 or 15 feet in the cold end of the drum followed by a gradual expulsion toward the hot end. Oxidation of iron salts is slower than that of copper salts. Solutions containing ferric sulphite have a red tinge, this fades and the solutions clear on complete oxidation to ferric sulphate. Special attention is called to chart D. As it was possible that the difficulty was caused by the large proportion of slimes in the pulp, a special run was made on 200-mesh Dorr underflow, the apparent recovery by leaching was 86.6 per cent.

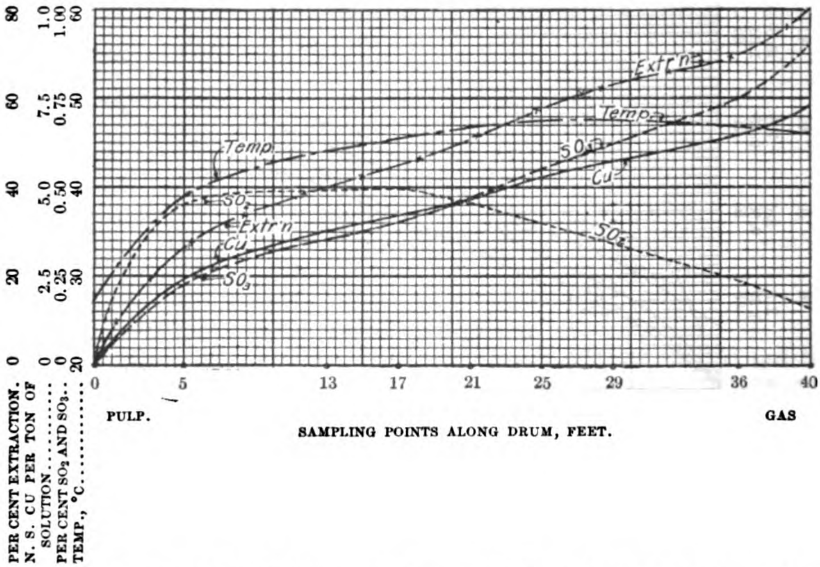

FIGURE 3.—Test B, May 28, 1919. Entering gas, SO_2, 1.48 per cent; temperature, 180° C.; exit gas, SO_2, 0.83 per cent; temperature, 37° C.; copper (n. s.) feed, 1.06 per cent; tails, 0.21 per cent; pulp density, 1.15; leaching extraction, 80.2 per cent.

The history of early leaching work under the Neill-Burfeind and subsequent patents indicates serious losses from reprecipitation of dissolved copper in the form of cupro-cupric sulphite. A careful study was made of leaching conditions as disclosed by sampling at 4-foot intervals. In no case was a chemical test for cupro-cupric sulphite obtained. As ammonia readily and completely dissolves this sulphite, many samples of the leaching-drum discharge were carefully washed, then leached with ammonia, but no evidence whatever of dissolution of copper was found. This test is effective only in the absence of copper carbonate and copper oxide minerals, as these are readily soluble in ammonia. In any properly conducted SO_2 leaching operation the copper carbonate and oxide would be completely dissolved early in the operation. Copper silicate was plainly visible in all these washed tailing samples when placed under the microscope and was occasionally discernible by the naked eye. Confirmatory tests were made by adding minute quantities of cupro-cupric sulphite to samples, when the ammonia solution quickly turned blue. Several samples were screened through 200-mesh and then the 200-product was separated by water sizing into sands and slimes. In each test copper silicate of the solid-solution type was found in the 200-mesh sand, many being distinguishable by the naked eye. Complete sets of samples taken along the length of the drum were sent to the Berkeley station and to the Salt Lake station of the Bureau of Mines. Microscopic and chemical tests showed copper silicate in each sample but no copper in sulphite form.

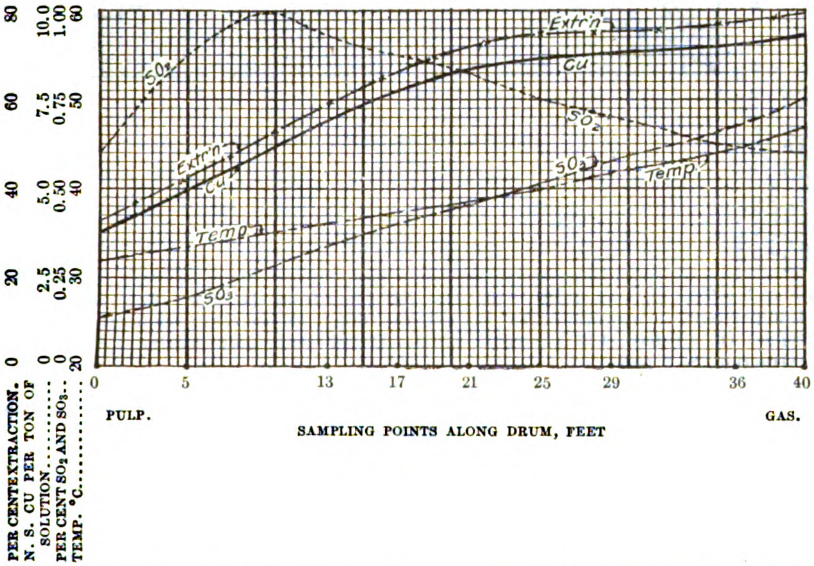

Figure 4.—Test C, July 13, 1919, with absorption tower. Entering gas, SO_2, 1.95 per cent; temperature, 252° C.; exit gas, SO_2, 0.83 per cent; temperature, 32° C.; copper (n. s.) feed, 1.11 per cent; tails, 0.23 per cent; leaching extraction, 79.3 per cent.

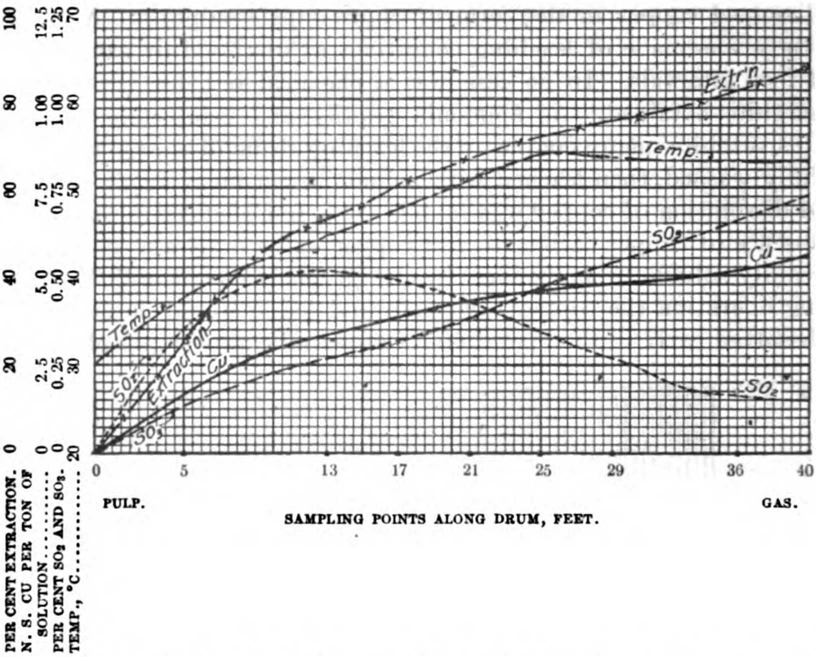

Figure 5.—Test D, August 19, 1919. Ore 200 slime from classifier. Entering gas, SO_2, 1.66 per cent; temperature, 274° C.; exit gas, SO_2, 1.12 per cent; temperature, 33° C.; copper (n. s.) feed, 1.27 per cent; tails, 0.17 per cent; pulp density, 2.85; leaching extraction, 86.6 per cent.

Table 2.—*Summary of monthly SO_2 leaching averages at Miami experimental plant.*

Date.	Ratio water solids.	Tons per 24 hours, average.	Per cent Cu (nonsulphide) leaching drum.		Apparent leaching extraction.	SO_2 gas.		Remarks.
			Feed.	Discharge.		Per cent SO_2.	Per cent absorption.	
1919.								
February	1.40	60	0.93	0.17	81.7	1.77	34	
March	1.32	90	.98	.29	70.0	1.82	40	
April	1.40	75	1.20	.33	72.5	1.70	50	
May	1.35	69	1.10	.32	70.9	1.48	50	
June	1.12	80	.90	.25	72.3	1.44	46	
July	1.14	100	1.09	.29	73.4	1.88	....	Absorption tower in use.
August	1.59	66	.94	.18	80.9	1.40	38	Slime with coarse sand removed.
September	1.34	80	.91	.19	79.5	1.65	40	
December	1.11	100	.94	.19	79.4	3.34	60	Aeration tail.
1920.								
January	1.08	100	.98	.20	79.6	4.26	61	
	With 42 pounds sulphuric acid per ton added at head of drum.							
Feb. 1 to 7	1.06	100	.96	.08	91.6	....	....	Aeration.
Feb. 8 to 15	1.12	100	.98	.10	89.8	....	....	No aeration.

It was thought that these resistant silicates might yield to longer leaching. It was also desirable to increase the SO_2 utilization, which was ranging at or slightly below 60 per cent. It seemed that both these objects might be attained by passing the cold pulp down an absorption tower countercurrent to the exit gas from the leaching drum. Accordingly, a 25-foot absorption tower, 3 by 3 feet in area, was introduced ahead of the drum. The pulp passed first into the absorption tower countercurrent to the cold exit gas from the drum, thence into the drum as usual. Comparative leaching results given below indicate that this pretreatment was of no value:

TABLE 3.—*Comparative leaching results with and without absorption tower.*

Condition.	Number of shifts.	Per cent copper (nonsulphide).		Apparent extraction, per cent.
		Feed.	Tailing.	
With tower	12	1.118	0.306	72.6
Without tower	11	.998	.276	72.3

Figure 4, test C, which records a run with the absorption tower, shows that the pulp absorbed practically 0.60 per cent SO_2 during its passage through the tower, but the extraction is no better than that shown in chart B in which the maximum absorption is under 0.50 per cent.

EXPERIMENTS BY C. M. BOUTON.

At the request of the Tucson experiment station, C. M. Bouton, physical chemist at the Berkeley station, was detailed during December, 1919, and January, 1920, to make a careful microscopic and chemical study of the ore and of leaching products at the Miami plant. Two brief quotations from his interesting report follow. The first deals with the possibility of losses from precipitation of sulphites, the second offers a general conclusion on the leaching operation:

> Cupro-cupric sulphite, a red crystalline precipitate, having the composition $Cu_2SO_3.CuSO_3.2\,H_2O$ forms quickly when sulphurous-acid solutions of copper are heated in open vessels. This compound tends to form in the discharge or hot end of the drum, as shown by the fact that a crust varying (according to report) from $\frac{1}{16}$ to $\frac{1}{8}$ inch was found coating the inside of that part of the drum after several months' run. The "drum discharge," indeed, is always colored more or less brightly red, but this is not evidence of the presence of cupro-cupric sulphite because ferric sulphite, a soluble salt, is quickly formed in presence of air and colors its solutions intensely red. The amount of cupro-cupric sulphite actually formed is very doubtful. It has never been identified as such in drum pulps by use of the microscope or by microchemical tests, although it commonly forms in a characteristic crystalline shape of four-pointed stars. Numerous red particles of iron oxide occur in the pulp and these render it impossible to depend on color alone for identification. Whenever these red particles have been tested microchemically they have shown the presence of much iron and no copper. Nevertheless, the possibility of loss of

copper from solution in this way would be a source of uneasiness were it not for the fact that cupro-cupric sulphite dissolves quite readily when suspended in slightly acid solutions and agitated by an air current. About one-half gram of cupro-cupric sulphite crystals, placed in a 200-c. c. glass cylinder with 150 c. c of clear leaching-drum solution and agitated vigorously with a jet of compressed air, disappeared entirely in the course of half an hour. Similarly placed and agitated in water the red crystals appeared unaffected even after two to three days' agitation. When similarly treated in a neutral solution of copper sulphate the crystals likewise appeared unaffected after several hours' agitation, but in the course of a day they appeared to have grown less in amount, while a light-yellow solid was found suspended in the solution. This is counter to a statement by Greenawalt[12] that cupro-cupric sulphite is quite soluble in a solution of copper sulphate. Cuprous sulphite, Cu_2SO_3, has been prepared in a white and in a red crystalline form, the chemical difference being in the amount of water of crystallization. * * * It is insoluble in water, but its sensitiveness to oxidizing influences renders it rather unstable. Both the acidic and basic parts of the molecule are subject to oxidation, but it is obvious that if the copper is to pass into solution in an oxidized condition another acidic radicle is necessary for each molecule of $CuSO_3$. Thus $CuSO_3$ would only pass into solution if acid were present. Unlike pure cuprous sulphite the cupro-cupric sulphite is very stable in air or in water, but in order for it to pass into solution the same reasoning applies to the cuprous part of its molecule. This explains the necessity for the presence of acid in dissolving the cupro-cupric sulphite. The conclusion may, therefore, be drawn that in solutions even faintly acid, with a low content of SO_2 and a plentiful supply of air, there is no risk of precipitation of copper as cupro-cupric sulphite. These are conditions abundantly realized in drum leaching at Miami.

The general conclusion reached is that the process is efficient as now operated and that a theoretically maximum efficiency is prevented by the existence of part of the copper in the form of resistant silicate minerals. No evidence was found that erratic recoveries were due to the existence of any critical or delicate adjustments in the regulable factors of the process. Moreover, there was no indication that the results were influenced by any obscure factors which had previously escaped notice. The one variable which vitally affected recoveries and which was not properly controlled was the composition of the ore. Sudden changes in the per cent recovery of oxide copper (i. e. oxide copper in heads minus oxide copper in tails divided by oxide copper in heads) were found to coincide with changes in the source of supply of ore. Average high recoveries or low recoveries persist over considerable periods, but show, however, minor fluctuations, so that it is exceedingly difficult to evaluate the metallurgical effect of adjustments in operating. This evaluation is rendered more difficult by the fact that a few hundredths of a per cent of copper is significant, an amount that is readily obscured by errors in sampling and in assaying. The storage bins of the experimental mill have a capacity of about 350 tons, so that they must be refilled every three or four days. While each lot may be considered as well mixed and the number of samplings over the 9 to 12 shifts of its passage through the mill is enough to overcome most of the errors of sampling and of assaying, it can not be assumed that the next lot will have the same proportion of the resistant copper silicates. A closer cooperation or understanding between mine and mill might help greatly in eliminating this uncertainty. As an example, the addition of a small amount of sulphuric acid to the drum discharge during a number of shifts was found to have extracted about onetenth of 1 per cent more copper from the aerator tails than were extracted by sulphurous acid alone. This comparison was based on the extraction of copper in absence of sulphuric acid for a number of shifts preceding the use of sulphuric acid. As a result of laboratory tests it appears probable that sulphuric acid actually improves the recovery of copper, but the above figure of 0.1 per cent is not a reliable index of the amount of improvement, because a change in the ore may have occurred during the period of this test.

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[12] Greenawalt, Wm. E., Hydrometallurgy of copper, 1912, p. 175.

The operation of the plant at Miami is to be regarded as experimentation on a large scale and the interpretation of results is impossible unless vital factors, such as the composition of the ore, are controlled with the same accuracy that is considered necessary and feasible in connection with small-scale experimentation. As pointed out above, under present conditions there is no guarantee that successive lots of ore will have the same composition as regards the copper minerals present. There are obvious difficulties in the way of securing closer control over the ore supply, but unless material of reasonably uniform composition can be obtained, erratic leaching results are to be expected. As yet no small-scale tests have been developed which will permit a ready classification of the ore as regards leaching behavior, and there is some question as to whether satisfactory tests for this purpose can be developed. Under these circumstances, the leaching plant is also the experimental laboratory, and it is, therefore, particularly vital that a supply of ore of constant composition be secured. Unless this can be done, erratic and uninterpretable results are to be expected.

RESULTS OF FLOTATION TESTS OF CEMENT COPPER.

The upper, sulphide, flotation plant was run in accordance with established practice and the results were uniformly satisfactory; the lower flotation plant, for the recovery of cement copper, gave very erratic results. Reoiling is necessary, as the flotation properties of the oils remaining in the upper flotation tailing are destroyed during passage through the leaching drum. The best results in floating cement copper were obtained by adding oil before precipitation. Various oils and combinations were tried. A creosote oil, high in phenol, seemed to give as good results as any. Sometimes pine oil was added in small quantities at the head end of the first cell when addition of a frothing agent seemed necessary. The coarse cement copper was readily floated, but the fine gave trouble. These difficulties may be attributed to three main reasons:

1. Sudden fluctuation in feed, as discussed on pages 29 and 30.

2. Improper precipitation. Precipitation on iron balls is quite efficient, but most of the cement copper is exceedingly fine. Microscopic examination indicates that much of it would pass a 1,000-mesh screen. Laboratory scale tests indicated that cement copper obtained by precipitation on sponge iron floated much better.

3. Presence of SO_2 or sulphites: Free SO_2, or SO_2 combined in the form of bisulphite even to the extent of 0.04 per cent may seriously affect flotation. The sulphites, whether present as normal

sulphites or as bisulphites, are not in themselves detrimental; but the bisulphites are quite unstable and during the violent agitation may dissociate, thus liberating SO_2 molecules at any point in the process prior to complete oxidation. This might happen during precipitation or in any flotation cell. Whenever flotation became unusually poor the recovery generally began in the fourth or lowest roughing cell; this is doubtless explained by the progressive removal by agitation and aeration of free SO_2 as indicated by Table 4, in which the total SO_2, free and combined as sulphite, is indicated at successive points in the process.

TABLE 4.—*Percentage of sulphites at different stages in process.*

Point at which sample was taken.	Per cent total SO_2, free and combined as sulphite.		
	Test A.	Test B.	Test C.
At leaching-drum discharge	0.37	0.38	0.56
At last aeration-cell discharge	.23	.26	.35
At precipitating-drum discharge	.23	.27	.35
At second flotation-cell discharge	.05	.03	.06
At third flotation-cell discharge	.01	.01	.02
At fourth flotation-cell discharge	.01	.01	.01

The addition of an oxidizer, such as K_2MnO_4 or MnO_2, to the pulp before precipitation, will insure complete oxidation of sulphites and will thus remove certain obstacles to flotation of precipitated cement copper. In case the solution entering the precipitation drum contains copper in the form of sulphites, this copper may be precipitated as sulphite on metallic iron in the drum. The addition of an oxidizer after precipitation would not remedy this condition.

The color of the pulp leaving the precipitation drum served as a good index to the degree of oxidation. When sulphites were present, the pulp was reddish, and no flotation resulted. The first flotation cell showed a dark-brown froth, probably ferric sulphite, which settled to a deep-red solution that contained no copper; the second cell showed a bright, lemon-yellow froth composed of an iron salt, probably the result of dissociation of the sulphites. With the disappearance of this lemon-yellow color, metallic copper began to float. Pilot tests on these special solutions were made in the laboratory in a small glass column with pneumatic type bottom; by aeration in the usual way the lemon-yellow color appeared after three and one-half minutes' aeration; this color gradually faded, indicating complete oxidation, in five minutes; the precipitated copper then floated. With the plant in nice adjustment and under experienced supervision, almost perfect flotation was at times obtained; recovery by shifts frequently averaged above 90 per cent of the precipitated copper. During the

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11 months' run the total average monthly recovery of cement copper varied from 54 per cent to 82 per cent. Experiments made at several places indicate that copper precipitated by sponge iron is much more susceptible to flotation than the very fine copper obtained under precipitation conditions in this experiment. There is warrant for the opinion that with balanced leaching conditions, uniform pulp flow, complete removal of SO_2 and sulphites in the pulp, and with sponge iron as a precipitant, to obtain good flotation would simply be a matter of adjustment and experiment with reagents.

SUSPENSION OF MIAMI EXPERIMENT.

The Miami tests stopped for these reasons: Table 2 shows that the nonsulphide copper lost in the tailing during the leaching period of September, 1919–January, 1920, inclusive, varied from 0.19 to 0.20 per cent and that the average apparent recovery was 79.5 per cent. The addition of 42 pounds of sulphuric acid, recorded under February operations, reduced the tailing loss to 0.08 per cent with aeration, and 0.10 per cent without aeration. It was quite evident that sulphuric acid is a better solvent than SO_2 is for the resistant type of solid solution of copper silicate. Table 5 presents daily leaching data by shifts during the last two months of operation.

TABLE 5.—*Daily report on operation of Miami SO_2 leaching drum for period December 2, 1919, to January 25, 1920.*

Date of shift.	Ratio, water to solids.	Per cent nonsulphide copper.							Sulphur dioxide gas.			
		Leaching heads.	Leaching tailing.	Pregnant solution leaving drum.			Aerator tailing.	Aerator solution.	Entering.		Exit.	
				Per cent copper.	Per cent SO_2.	Temperature °C.			Per cent SO_2 by volume.	Temperature °C.	Per cent SO_2 by volume.	Temperature °C.
Dec. 2 A.......	1.08	0.76	0.12	0.506	0.53	47	......	......	2.70	228	1.30	......
B.......	1.08	.75	.15	.476	.69	46	......	......	2.45	......	.72	......
C.......	1.07	.75	.17	.525	.60	46	......	......	2.65	......	.68	......
3 A.......	1.20	.85	.19	.530	1.00	39	......	......	2.78	244	.81	18
B.......	1.06	.87	.15	.542	.76	42	0.12	0.594	2.78	254	.98	18
C.......	1.04	.83	.17	.618	.66	44	.12	.678	3.09	258	1.00	18
4 A.......	1.07	.81	.13	.561	1.00	40	.13	.560	3.40	239	1.84	19
B.......	1.11	.82	.11	.514	.80	43	.11	.580	3.24	250	1.64	17
C.......	1.08	.83	.17	.514	.71	41	.13	.577	3.16	254	1.61	17
5 A.......	1.12	.83	.16	.477	.84	41	.14	.536	3.42	244	1.85	19
B.......	1.21	.83	.16	.528	.61	45	.13	.629	3.34	250	2.00	21
C.......	1.02	.81	.17	.548	.57	45	.14	.628	3.34	252	2.02	21
6 A.......	1.02	.75	.27	.541	.83	45	.21	.618	3.39	253	......	21
B.......	1.07	.84	.25	.531	.69	46	.18	.648	2.84	268	......	21
C.......	1.08	.87	.32	.508	.62	46	.21	.542	2.89	266	......	20
7 A.......	1.12	.95	.22	.480	.80	45	.20	.500	3.09	253	1.48	20
B.......	1.20	1.08	.25	.513	.98	41	.21	.617	3.09	260	1.55	20
C.......	1.20	1.05	.28	.448	.97	40	.24	.530	2.74	258	1.55	19
8 A.......	1.12	.93	.23	.500	.94	40	.18	.594	3.00	237	1.64	20
B.......	1.12	.71	.19	.454	.90	40	.15	.533	3.09	253	1.48	18
C.......	1.16	.66	.13	.415	.86	40	.10	.492	2.54	254	1.48	18
9 A.......	1.16	.71	.10	.414	.80	42	.08	.522	2.94	236	.95	16
B.......	1.19	.69	.07	.422	.84	42	.06	.464	3.19	260	1.55	17
C.......	1.20	.64	.10	.393	.81	42	.08	.447	3.09	261	1.50	18
10 A.......	1.16	.78	.14	.443	.80	42	.12	.466	2.95	236	.95	16
B.......	1.20	.61	.15	.400	.88	42	.14	.520	3.19	260	1.55	17
C.......	1.20	.58	.15	.328	.81	42	.12	.422	3.09	261	1.50	18

TABLE 5.—*Daily report on operation of Miami SO_2 leaching drum for period December 2, 1919, to January 25, 1920*—Continued.

Date of shift.	Ratio, water to solids.	Per cent nonsulphide copper.							Sulphur dioxide gas.			
		Leaching heads.	Leaching tailing.	Pregnant solution leaving drum.			Aerator tailing.	Aerator solution.	Entering.		Exit.	
				Per cent copper.	Per cent SO_2.	Temperature °C.			Per cent SO_2 by volume.	Temperature °C.	Per cent SO_2 by volume.	Temperature °C.
Dec. 11 A	1.17	0.57	0.13	0.335	0.84	41	0.10	0.371	3.09	255	1.10	17
B	1.16	.55	.16	.379	.83	42	.15	.488	3.09	265	1.33	17
18 B	1.26	.91	.27	.180	.95	34	.36	.252	3.09	221	1.95	14
C	1.16	.95	.27	.506	.98	35	.36	.556	3.50	230	1.30	12
19 A	1.12	.95	.26	.402	.96	35	.26	.387	3.00	204	1.17	21
B	1.12	.93	.24	.544	.78	37	.24	.392	2.92	240	1.72	20
C	1.09	.99	.26	.483	.89	37	.22	.578	3.50	240	1.30	17
20 A	1.02	.96	.30	.478	1.09	37	.27	.596	3.69	243	1.53	19
B	.98	.95	.29	.465	.47	38	.26	.549	4.01	248	1.60	20
C	1.01	.95	.16	.463	.90	37	.12	.553	3.76	249	1.04	20
21 A	1.11	.91	.27	.491	.92	38	.23	.480	3.00	210	1.30	19
B	1.08	.91	.29	.535	.91	37	.24	.605	3.76	241	1.29	18
C	1.10	.99	.27	.500	.81	35	.22	.590	3.90	246	1.17	17
22 A	1.12	1.00	.25	.492	.99	36	.25	.524	3.56	244	1.46	18
B	1.15	1.07	.31	.511	.94	35	.27	.605	4.05	241	1.27	19
C	1.11	1.01	.31	.504	.95	36	.25	.620	3.62	245	1.25	18
23 A	1.16	1.01	.26	.496	.98	35	.21	.623	3.83	245	1.07	19
B	1.15	1.05	.27	.556	.95	35	.23	.633	4.03	245	.97	18
C	1.11	1.04	.21	.593	.98	37	.17	.664	3.90	242	1.28	19
24 A	1.11	1.03	.20	.469	.98	35	.21	.609	4.20	238	1.51	20
B	1.12	1.02	.23	.520	.98	35	.23	.617	4.12	239	1.32	20
26 B	1.14	.94	.21	.504	.40	30	.25	.351	2.76	209	1.71	17
C	1.14	.96	.19	.550	1.00	35	.12	.546	3.76	227	1.71	17
27 A	1.14	1.03	.27	.513	1.00	35	.20	.570	3.97	250	1.61	20
B	1.11	1.13	.36	.521	1.02	37	.32	.610	4.00	257	2.25	20
C	1.07	1.08	.38	.535	.83	38	.23	.656	3.50	258	.84	17
28 A	1.23	1.07	.27	.506	.93	39	.25	.604	3.62	254	1.65	20
B	1.16	1.04	.41	.540	.96	38	.18	.572	3.76	255	1.74	18
C	1.14	1.03	.31	.538	.97	34	.16	.516	3.50	227	.75	21
29 A	1.08	.97	.24	.444	.93	36	.13	.626	3.51	247	1.17	19
B	1.10	1.09	.28	.559	.95	38	.16	.687	3.09	238	1.59	22
C	1.05	1.09	.27	.536	.81	40	.19	.667	3.62	238	1.42	20
30 A	1.06	1.05	.28	.540	.95	37	.21	.706	3.62	240	1.48	18
B	1.15	1.04	.32	.504	.94	37	.23	.695	3.10	220	1.28	22
C	1.06	1.07	.31	.526	.82	40	.21	.677	3.19	225	1.40	20
31 A	1.08	1.07	.31	.520	.90	37	.25	.657	3.19	231	1.04	20
B	1.14	1.04	.29	.502	.96	39	.24	.706	3.19	230	1.15	19
C	1.10	1.08	.25	.524	.72	40	.27	.693	3.19	228	1.37	20
Jan. 1 A	1.08	.99	.35	.517	.86	40	......	.671	3.29	227	1.33	19
B	1.00	.97	......	.553	.78	39	......	.705	3.29	237	1.67	20
C	1.05	1.04	.34	.520	.90	37	.26	.700	3.45	246	1.00	20
2 A	1.07	.97	.28	.527	.85	37	.28	.704	3.29	245	1.38	20
B	1.02	.99	.29	.539	.90	40	.16	.713	3.41	247	1.67	19
C	1.08	.99	.27	.487	.75	39	.14	.653	3.56	247	1.18	19
3 A	1.23	.99	.33	.507	.95	37	.29	.679	3.39	246	1.25	20
B	1.00	1.00	.31	.560	.83	40	.22	.746	3.62	245	1.73	20
C	1.02	1.05	.34	.551	.98	37	.25	.710	3.50	244	1.37	19
4 A	1.18	1.03	.26	.535	.87	37	.25	.685	3.50	242	1.37	20
B	1.09	1.02	.30	.500	.94	39	.27	.701	3.76	245	1.78	20
C	1.07	1.01	.28	.538	.90	38	.13	.678	3.97	244	1.44	20
5 A	1.14	1.01	.25	.564	.98	38	.15	.771	3.62	244	1.40	20
7 B	1.06	.93	.35	.478	1.08	33	.27	.607	3.19	220	.83	14
C	1.15	.88	.27	.354	1.09	34	.24	.619	4.05	234	1.52	15
8 A	1.17	1.04	.19	.454	.98	35	.09	.720	3.62	225	1.77	15
B	1.14	1.07	.28	.565	.93	35	.20	.756	3.62	207	1.57	15
C	1.12	1.13	.27	.520	.98	35	.14	.754	3.76	203	1.78	15
9 A	1.12	1.09	.32	.620	1.00	35	.21	.798	3.70	214	1.87	17
B	1.08	1.11	.33	.630	1.06	35	.25	.780	4.20	230	2.15	17
C	1.10	1.14	.30	.629	1.12	34	.25	.760	4.05	209	2.02	12
10 A	1.18	1.03	.18	.610	.98	33	.15	.745	4.05	228	1.68	13
B	1.05	1.03	.33	.592	.92	34	.21	.745	3.65	219	1.71	14
C	1.03	1.03	.27	.619	1.10	35	.19	.809	4.20	225	2.08	14
18 B	1.20	1.09	.29	.533	1.30	30	.27	.555	4.20	218	1.03	13
C	1.12	1.01	.23	.653	1.19	33	.20	.665	4.25	226	1.07	15
19 A	1.08	1.01	.26	.550	1.12	33	.26	.650	4.67	220	1.25	11
B	1.05	1.02	.23	.603	1.03	35	.21	.662	4.68	206	1.78	......
C	1.11	1.04	.23	.485	1.01	35	.26	.680	4.46	201	2.00	......

TABLE 5.—*Daily report on operation of Miami SO_2 leaching drum for period December 2, 1919, to January 25, 1920*—Continued.

Date of shift.	Ratio, water to solids.	Per cent nonsulphide copper.							Sulphur dioxide gas.			
		Leaching heads.	Leaching tailing.	Pregnant solution leaving drum.			Aerator tailing.	Aerator solution.	Entering.		Exit.	
				Per cent copper.	Per cent SO_2.	Temperature °C.			Per cent SO_2 by volume.	Temperature °C.	Per cent SO_2 by volume.	Temperature °C.
Jan. 20 A	1.06	0.99	0.24	0.589	1.17	35	0.24	0.644	4.29	200	1.53	....
B	1.04	1.01	.24	.591	1.08	36	.22	.639	4.68	199	1.75	....
C	1.08	1.11	.28	.660	1.05	36	.25	.678	4.57	198	1.78	....
21 A	1.00	1.02	.23	.658	1.13	37	.23	.797	5.05	190	1.98	....
B	1.11	.92	.17	.611	1.11	36	.17	.689	5.68	214	1.84	....
C	1.09	.90	.17	.661	1.05	36	.15	.755	5.55	213	1.98	....
22 A	.94	.85	.16	.600	1.32	37	.14	.748	5.59	212	1.89	....
B	1.07	.85	.15	.666	1.23	37	.15	.715	6.00	211	1.45	....
C	1.08	.85	.13	.695	1.18	36	.15	.731	5.95	210	1.61	....
23 A	.93	.84	.21	.615	1.07	37	.13	.719	4.68	189	2.06	....
B	1.04	.84	.23	.567	1.02	37	.17	.705	4.67	200	1.73	....
C	1.11	.85	.19	.602	1.01	37	.11	.699	4.55	202	1.76	....
24 A	1.00	.85	.23	.602	1.08	37	.21	.680	4.59	196	1.72	....
B	1.01	.87	.19	.597	1.09	37	.19	.689	4.68	214	1.78	....
C	1.04	.96	.22	.615	1.05	36	.21	.692	4.59	215	1.87	....
25 A	1.06	.92	.19	.538	1.15	37	.16	.666	4.91	211	2.39	....
B	1.06	.91	.19	.599	1.11	36	.17	.677	4.68	215	2.03	....
C	1.11	.93	.18	.632	1.12	37	.17	.725	5.03	217	2.00	....
SUMMARY—AVERAGES BY PERIODS.												
Dec. 2-11, 1919	1.126	0.783	0.172	0.4773	0.792	42.6	0.142	0.5422	3.022	252.2	1.386	18.5
Dec. 18-27, 1919	1.112	.991	.264	.4911	.902	35.8	.238	.5486	3.643	238.0	1.401	18.3
Dec. 28-31, 1919	1.112	1.053	.295	.5199	.903	37.9	.207	.6505	3.382	236.1	1.337	19.9
Jan. 1-10, 1920	1.093	1.023	.290	.5404	.947	36.5	.209	.7170	3.665	232.2	1.564	17.5
Jan. 18-25, 1920	1.061	.942	.210	.6554	1.116	35.7	.192	.6895	4.866	207.7	1.751	....
Average, Dec. 2 to Jan. 25, inclusive	1.101	.958	.246	.5368	.932	37.7	.197	.6295	3.716	233.2	1.488	18.5

While the Miami SO_2 leaching experiment was in progress the Inspiration Consolidated Copper Co. erected a 30-ton experimental sulphuric-acid leaching plant. The two mines adjoin each other and the ores are much alike. The Inspiration ores contain a negligible proportion of soluble iron and hence have the advantage over the ores being treated by sulphuric-acid leaching at the New Cornelia Copper Co. plant at Ajo, Ariz. The Inspiration research staff did not venture far outside of known practice; it took full advantage of available knowledge on the subject, with the result that it greatly simplified procedure and worked out what seems to be a highly efficient and economical sulphuric-acid leaching process. Decided advance was made in electrolysis. Absence of impurities in the Inspiration ore permits the use of a very dilute electrolyte containing about 1 per cent copper as against 3 per cent copper at Ajo. Furthermore, it was found possible to strip the discard solutions by electrolysis, thus avoiding the necessity of precipitation on iron, the entire product being electrolytic copper.

The fact that results at Inspiration were much better than those at Ajo interested the Miami Copper Co. to the point of deciding to undertake similar experiments on its ores, except that the ore leached was to be finely ground ore (48-mesh), not coarse (¼-inch), as at Inspiration. This involved investigating the possibilities of filtration of acid pulp, and it was decided to suspend experimental work on SO_2 leaching. The Miami Copper Co.'s experimental campaign on sulphuric-acid leaching was prematurely interrupted by the general depression of copper mining.

COOPERATIVE WORK WITH ARIZONA COPPER CO.

Experimental work begun in 1917 by the Arizona Copper Co. on mixed ores and tailings led that company to build a 10-ton experimental sulphuric-acid leaching plant at Clifton. This plant and its operation on old tailings were described in the Engineering and Mining Journal.[13] Early in 1918 old tailings accumulated by the Detroit Copper Co., the Shannon Copper Co., and the Arizona Copper Co. were tested in the Tucson SO_2 leaching drum. The results were encouraging enough to induce the Arizona Copper Co. to consider erecting a small drum in connection with its sulphuric-acid leaching experiment. After some delay this project was carried out; a 5 by 20 foot leaching drum following the Tucson design and a 4-foot, 6-hearth roasting furnace were fitted into the old experimental sulphuric-acid leaching plant. Leaching with SO_2 began in June, 1920, and went on intermittently until April 1, 1921.

OLD TAILINGS TREATED.

In this discussion reference is made to three distinct accumulations of old tailings. The accumulations differ appreciably as to proportion of sand and slimes, chemical composition, and copper content, as will be noted from the following tabulation:

TABLE 6.—*Characteristics of old tailings.*

	Per cent copper.		Acid consumed, pounds H_2SO_4 per ton.
	Sulphide Cu.	Nonsulphide Cu.	
Morenci old mill tailings	0.32	0.58	83
Clifton old mill tailings	.38	.90	64
Shannon old mill tailings	.64	.60	150

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[13] Crowfoot, Arthur, and Donaldson, Kenneth H., Leaching and concentrating mixed ores. Eng. and Min. Jour., Sept. 4, 1920, vol. 110, p. 471.

The aggregate quantity of these tailings is, roughly, 8,000,000 tons. The Clifton deposit is described as follows:

> The deposit consists of a mixture of practically untreated "oxide" slime and the slime tailings from a sulphide mill. The "oxide" slime originated in a concentrating plant which preceded the old leaching plant at Clifton, the "oxide" ore being treated in a Hancock jig for the removal of a coarse concentrate before leaching. The slime was then removed from the jig middling and sent direct to the ponds without further treatment. The deslimed jig middling was sent to the leaching plant. (See Greenawalt's "Hydrometallurgy of copper," p. 183.) The tailing from the sulphide mill was desanded by the use of a special form of elevator, the slime joining the "oxide" slime in the ponds and the sand being hauled away in railroad cars to form the banks of the ponds and for other purposes.
>
> The banks of these tailing ponds are constructed of tailing sand having a maximum size of grain of between 1.5 and 2 mm., and 93 per cent of the material in the ponds is fine enough to pass through a 200-mesh sieve which has openings 0.074 mm. square. The sandy material forming the banks of the ponds constitutes only a small percentage of the total deposit, and this material was not included in the feed to the test plant. The copper in this sandy material will, however, be readily amenable to recovery by the same flow sheet proposed for the treatment of the slime.
>
> The slime mixture as it occurs in the ponds has the appearance of a stiff clay and contains 20 per cent by weight of moisture. The material settles slowly, average results showing that about 30 square feet of settling area is required per dry ton of material to obtain a Dorr tank underflow with a density of 50 per cent solids, as was required. Large tank areas are therefore necessary. For instance, to settle 100 tons of the slime from a density of about 25 per cent solids (the density leaving flotation cells) to a density of 50 per cent solids a tank 60 feet in diameter is required.

Generally speaking, the Clifton tailing constitutes the simplest and the Shannon tailing the most difficult leaching problem of the three. The Arizona Copper Co. did most of its work on sulphuric-acid leaching with the Clifton tailing, making only one run on the Morenci tailing. When SO_2 leaching was undertaken by this company it began with Morenci tailings. Next the Shannon tailings dump was tested. This work was in progress at the time of the general suspension of operations in the copper industry. When the run on Shannon tailings was completed the test plant closed down. Therefore the only direct comparison available between sulphuric-acid leaching and SO_2 leaching is on Morenci tailings. Comparative work was done subsequently at Tucson after the closing of the Clifton experimental plant.

TABLE 7.—*Sulphuric acid leaching results on Clifton old mill tailings and Morenci old mill tailings, with comparative SO_2 leaching results, by periods, on Morenci old mill tailings.*

Products.	Clifton old mill tailings H_2SO_4 leaching (1919).		Morenci old mill tailings.					
	First test.	Second test.	H_2SO_4 leaching (1920).	SO_2 leaching by periods.[a]				
				A.	B.	C.	D.	E.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
24-hour days in period	......	......	......	94	6	26	24	13
Hours in period	......	......	......	2,256	144	624	576	312
Flow sheet used	1	1	1	1	1	2	3	3
Tube-mill feed:								
Dry tons treated	......	......	1,892	2,279	66	295	475	309
Assay per cent total Cu	1.36	1.31	1.02	0.76	0.75	0.82	0.93	0.85
Assay per cent acid-sol. Cu	.79	.84	.59	.43	.34	.43	.54	.50
Assay per cent water-sol. Cu	.13	.19	......	......	......	......	......	......
Assay per cent sulphide Cu	.44	.28	.43	.33	.41	.39	.39	.35
Lixiviating drum feed:								
Assay per cent total Cu	......	......	......	.73	.70	.87	.55	.57
Assay per cent acid-sol. Cu	......	......	......	.37	.28	.50	.46	.45
Assay per cent sulphide Cu	......	......	......	.36	.42	.37	.09	.12
Pulp temp., (° C)	......	......	......	30	24	23	14	12
Lixiviating drum discharge:								
Pulp temp. (° C)	......	......	......	41	45	43	42	37
SO_2 in pulp (per cent)	......	......	......	.75	.34	.29	.52	.73
Aerating tank discharge:								
SO_2 in pulp (per cent)	......	......	......	.12	.09	.05	.07	.06
Pulp ratio	......	......	......	1.08:1	1.66:1	1.42:1	1.03:1	0.95:1
Cu in solution (per cent)	......	......	......	.20	.19	.30	.33	.29
Cu in washed residue (per cent)	......	......	......	.54	.51	.55	.23	.25
Roaster data:								
Per cent concentrate fed (dry pounds)	......	......	......	172,206	13,450	58,550	69,500	30,700
Sulphur in calcine (per cent)	......	......	......	7.13	6.07	5.34	5.66	6.67
Gas temp. (° F)	......	......	......	580	625	634	580	562
SO_2 in gas to drum (per cent)	......	......	......	2.99	2.55	2.83	2.95	3.66
SO_2 in gas from drum (per cent)	......	......	......	1.23	1.50	1.70	1.84	2.19
Absorption SO_2 (per cent)	......	......	......	58.86	41.18	39.93	37.63	40.16
Acid consumption:								
Pounds added per dry ton treated	59.08	60.01	83.15	......	......	......	......	......
Pounds added per lb. total Cu	2.17	2.29	4.08	......	......	......	......	......
Pounds added per lb. a. s. Cu	3.74	3.58	7.05	......	......	......	......	......
Pounds added per lb. a. s. Cu recovered	4.40	4.21	8.00	......	......	......	......	......
Flotation feed:								
Assay per cent total Cu	1.43	1.37	.85	.82	.73	.80	.88	.87
Assay per cent acid-sol. Cu	.23	.25	.17	.20	.12	.14	.58	.55
Assay per cent water-sol. Cu	.73	.74	.27	.28	.28	.27	......	......
Assay per cent sulphide Cu	.47	.38	.41	.34	.33	.39	.30	.32
Flotation tailing:								
Assay per cent total Cu	.90	.94	.42	.61	.26	.54	.54	.57
Assay per cent acid-sol. Cu	.12	.17	.14	.15	.07	.10	.45	.45
Assay per cent water-sol. Cu	.69	.70	.17	.25	.14	.19	......	......
Assay per cent sulphide Cu	.09	.07	.11	.21	.05	.25	.09	.12
Flotation concentrate:								
Assay per cent total Cu	10.18	8.50	3.86	3.53	2.35	1.93	5.74	3.27
Assay per cent acid-sol. Cu	.94	1.71	1.56	1.19	.72	.77	1.38	1.24
Assay per cent sulphide Cu	9.24	6.79	2.30	2.34	1.63	1.16	4.36	2.03
Ratio of concentrate, tons into 1	......	......	8.00	13.9	4.5	5.4	15.3	8.3
Oliver filter cake (waste tailing):								
Assay per cent total Cu	.22	.23	.19	.35	.19	.35	.25	.28
Assay per cent acid-sol. Cu	.10	.12	.08	.13	.06	.09	.10	.09
Assay per cent water-sol. Cu	.05	.04	......	......	......	......	.04	.06
Assay per cent sulphide Cu	.07	.07	.11	.22	.13	.26	.11	.13
Extraction (waste tailing):								
Of total Cu recovered (per cent)	84.57	83.2	83.59	53.95	79.88	63.89	77.34	71.19
Of total sulphide Cu recovered (per cent)	82.70	76.4	77.39	33.33	75.24	44.27	75.56	73.45
Acid-sol. Cu recovered (per cent)	84.93	85.1	88.12	69.77	85.35	81.89	78.61	67.97
Over-all extraction (based on 0.01 per cent water-sol. Cu in Oliver filter cake):								
Total Cu recovered (per cent)	84.57	83.2	83.59	53.95	79.88	63.89	77.42	75.30
Sulphide Cu recovered (per cent)	82.70	76.4	77.39	33.33	75.24	44.27	75.56	73.45
Nonsulphide Cu recovered (per cent)	84.93	85.1	88.12	69.77	85.35	81.89	81.48	82.00

[a] 1920.

A. June 1-Sept. 2, flow sheet 1.
B. Sept. 2-Sept. 8, flow sheet 1, total circulating load (including new ore) reduced to 20 tons.
C. Sept. 10-Oct. 5, flow sheet 2.
D. Oct. 8-Oct. 31, flow sheet 3, X-cake flotation.
E. Nov. 1-Nov. 13, flow sheet 3, oil flotation.

Experimental work is often greatly handicapped by inadequate or makeshift apparatus. It is difficult to overcome a reluctance to spend a large sum of money for short-time experiments when an expenditure of perhaps one-quarter of the sum indicated will seemingly give approximate results that may later be followed by experiments on a larger or perhaps a semicommercial scale. The work described here was not an exception to this rule. The equipment was scattered and was operated at different levels of the mill. Part of the power was transmitted from shafting from the main concentrator. It was admittedly a "makeshift" plant and in many ways was poorly adapted to do the work expected of it.

FLOW SHEETS.

Three different flow sheets were used during the SO_2 leaching tests. The first one corresponds to the flow sheets used during the sulphuric-acid leaching campaign. The other two are radically different. Table 7 gives all the comparative data available on the earlier and the later sulphuric-acid leaching tests and on the SO_2 leaching work, which latter is reported by periods with foot notation stating type of flow sheet used.

The flow sheets used during tests 1 and 2, both sulphuric-acid leaching tests of Clifton tailings, differ in one respect. In test 1 the leached pulp was filtered and washed, the washed cake being repulped with water for flotation; in test 2 the sulphide flotation was carried on in copper sulphate solution. In test 3, sulphuric-acid leaching of Morenci tailings, and in tests 4 to 6, inclusive, SO_2 leaching tests of Morenci tailings the flotation was in copper sulphate solution; in tests 7 and 8 the flow sheet was changed to preflotation.

FLOW SHEET 1.

In flow sheet 1 (Fig. 6), the SO_2 drum and aerating tanks are in closed circuit with the tube mill and classifier; as a result, the sands removed by the belt drag and returned to the circuit built up in the drum so much that the circulating load was several times the new feed tonnage. This overload prevented proper contact between fresh pulp and reagent, and overtaxed the aerating tanks so that the pulp contained too much SO_2 for satisfactory flotation. The average extraction during this run was: Nonsulphide copper, average over-all extraction, 69.77 per cent; sulphide copper, 33.30 per cent.

For a six-day period the tonnage was reduced to the point where the circulating load through the drum, including the original feed,

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did not exceed 25 tons. The extraction increased noticeably, the average over-all extraction of nonsulphide copper rising to 85.35 per cent, and that of sulphide copper to 75.24 per cent. The following results of sulphuric-acid leaching tests on the same general flow sheet are offered for comparison: In a 61-day run on Morenci old-mill tailing, 24 tons daily, the over-all recovery of nonsulphide copper was 81.89 per cent, and of sulphide copper 77.32 per cent; the consumption of acid was 6.2 pounds.

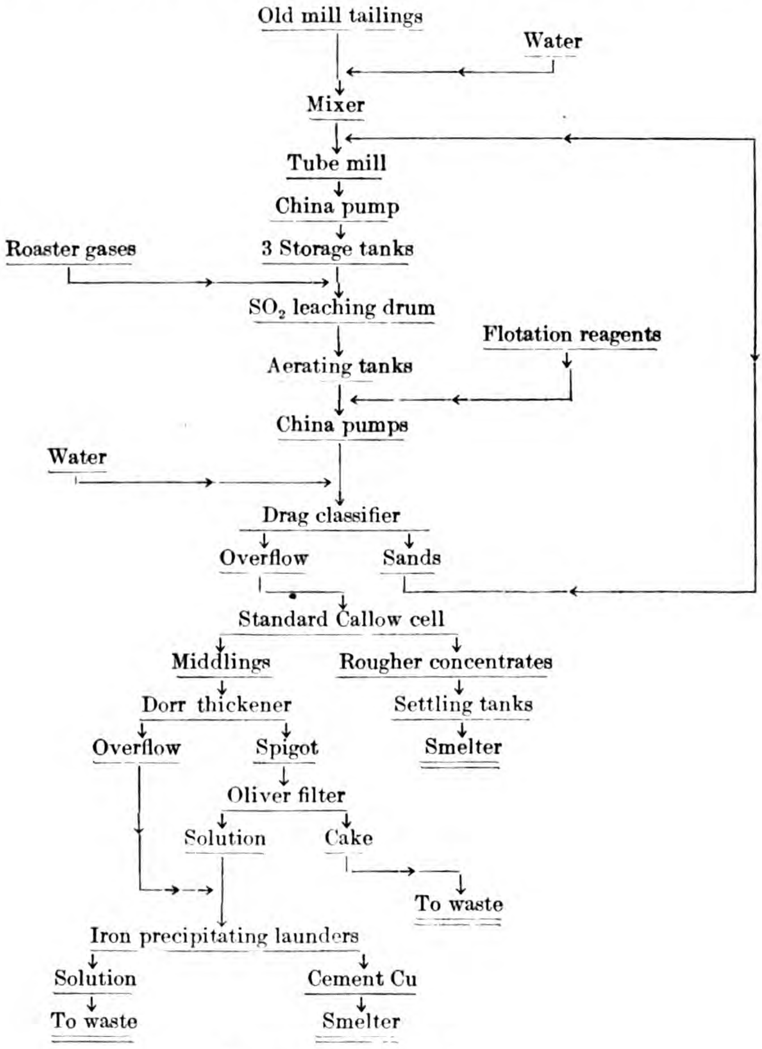

FIGURE 6.—Flow sheet 1.

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FLOW SHEET 2.

Flow sheet 2, (Fig. 7) differs from flow sheet 1 in that the leaching drum and aerating tanks were removed from the closed circuit of tube mill and classifier. Three tanks, formerly used as sulphuric-acid leaching tanks, were used as thickeners for SO_2 leaching pulp.

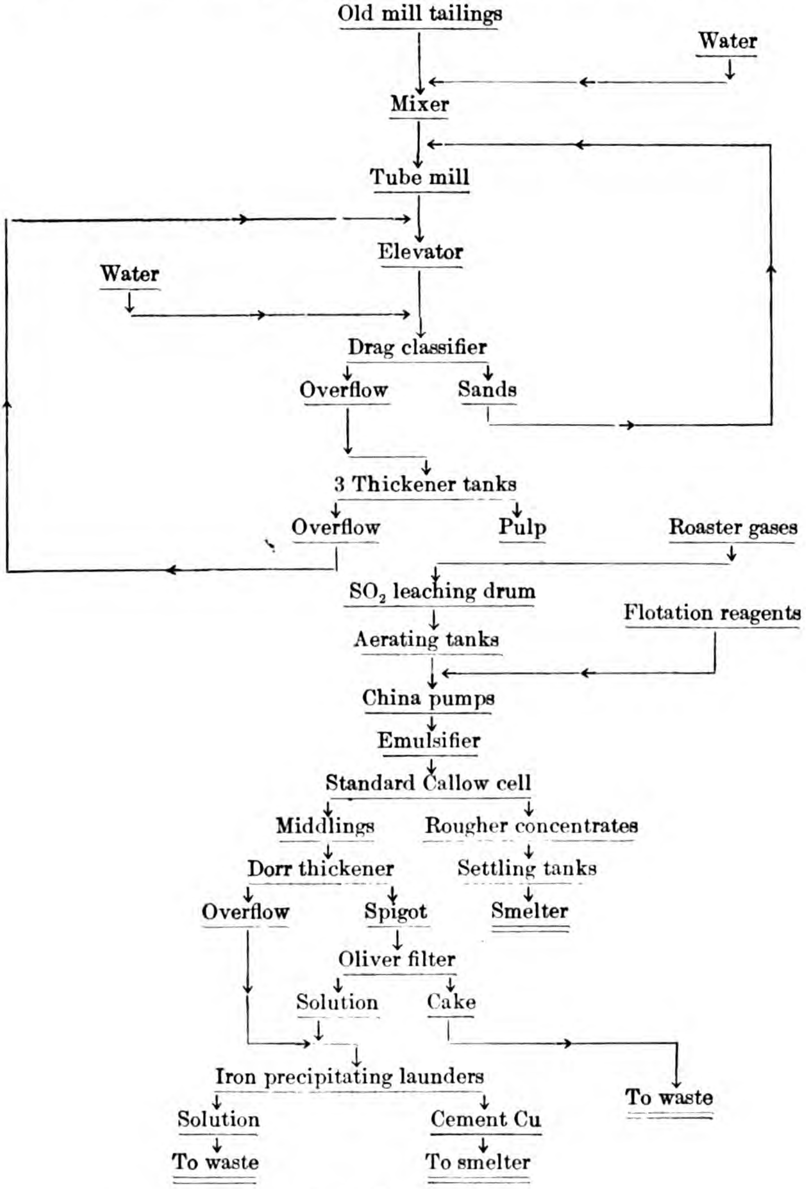

FIGURE 7.—Flow sheet 2.

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They proved unsatisfactory because of the difficulty in controlling the density of the underflow; in consequence the density of the drum feed and of the flotation pulp were irregular. As in flow sheet 1, flotation follows leaching. On a 26-day run on Morenci old-mill tailing (see Table 6 for copper content) the following over-all extraction was obtained by SO_2 leaching: Nonsulphide copper, 81.89 per cent; sulphide copper, 44.27 per cent. The poor sulphide flotation is partly accounted for by the fluctuation in pulp density. The SO_2 gas consumed during this run, figured as 100 per cent H_2SO_3, amounts to 51 pounds per ton of ore, equivalent to 4.3 pounds per pound of Cu recovered. Former sulphuric-acid leaching work consumed 64 pounds, 100 per cent H_2SO_4, with an over-all nonsulphide recovery of 88.12 per cent, equivalent to 6.2 pounds of acid consumed per pound of Cu recovered; the slightly lower recovery by SO_2 is probably due to insufficient absorption and utilization of SO_2. With the installation of satisfactory thickening tanks to insure regularity of feed density, no reason is apparent why the satisfactory results recorded for the short six-day run under flow sheet 1 should not be equaled.

FLOW SHEET 3.

Flow sheet 3 (Fig. 8) is designed for preflotation of sulphides. The leaching campaign on Morenci tailing with plant arrangement according to flow sheet 3 is divided into two periods. First (D, Table 7), a 24-day run, daily tonnage 24 tons, X-cake as flotation reagent, in which the over-all recovery of nonsulphide copper was 81.48 per cent, and of sulphide copper 75.56 per cent. This was followed by (E, Table 7) a 13-day run, same daily tonnage, flotation oils, in which the over-all recovery of nonsulphide copper was 82.00 per cent and of sulphide copper 73.45 per cent. The absorption of SO_2 in the leaching drum stated in terms of 100 per cent H_2SO_3 was 43 pounds for D and 36 pounds for E per ton of ore.

DISCUSSION OF TESTS OF MORENCI TAILINGS.

Columns 3 and 5, Table 7, give results of sulphuric-acid leaching and of SO_2 leaching with practically the same general flow sheet. The consumption of SO_2, stated in terms of 100 per cent H_2SO_3, is 67 pounds per ton of ore, and of 100 per cent H_2SO_4 64.6 pounds. The extraction slightly favors sulphuric-acid leaching, 88.12 as against 85.35 per cent. Judged with regard to cost of reagent, however, the comparison decidedly favors SO_2. Cost estimates for sulphuric-acid leaching in this territory are generally made on the basis of 60° B. acid costing $10 per ton f. o. b. point of consumption, as this is the grade of acid made at Douglas. In the sulphuric-acid leaching above recorded the acid consumption is 8 pounds of 60° acid per pound of Cu recovered, making the acid cost 4 cents per pound of Cu recovered. With an 88.12 per cent extraction the yield of copper is 10.4 pounds of Cu per ton; total cost of sulphuric acid, \$0.415 per ton.

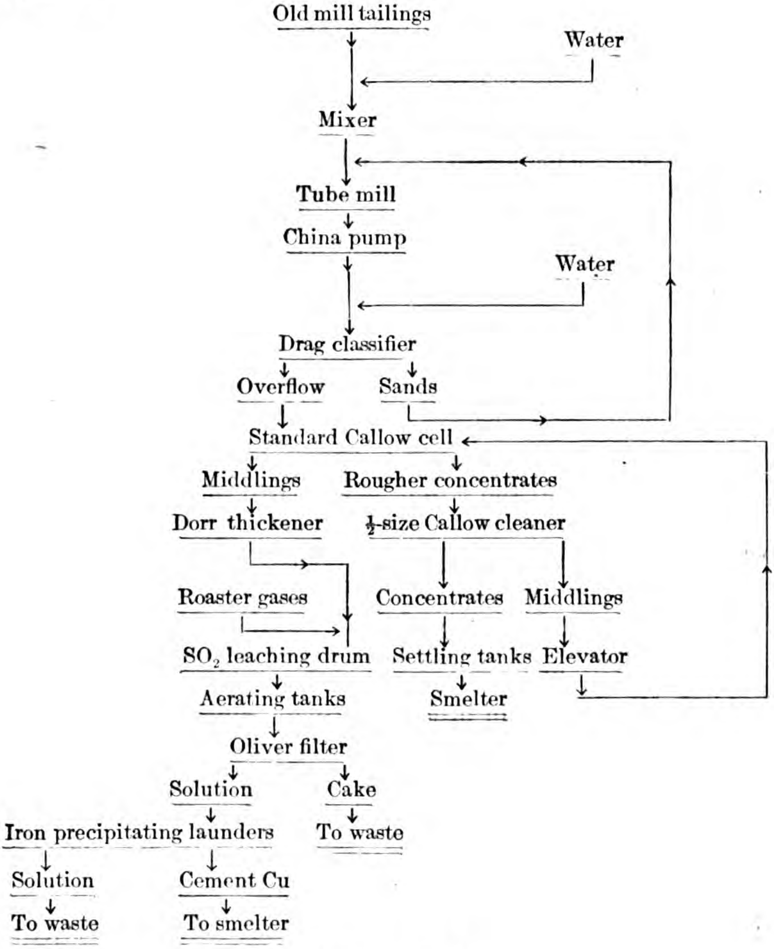

FIGURE 8.—Flow sheet 3.

Based on the Clifton operations, the Arizona Copper Co. estimates that the cost of producing SO_2 by roasting concentrates, figured in terms of 100 per cent H_2SO_3, is \$1.20 per ton or 0.06 cents per pound of acid. The consumption of H_2SO_3 in the test recorded above is 6.65 pounds per pound of Cu, or 67 pounds per ton of ore. The cost of acid per ton of ore, then, would be 4.5 cents. Sulphuric-acid leaching shows a higher recovery by 0.32 pounds Cu per ton. At

15 cents per pound the value of this copper is 4.8 cents per ton treated, and this amount should properly be added to the cost of reagent in SO_2 leaching to give a basis for comparison. The comparative cost of reagent per ton would then be: H_2SO_4 leaching, 41.5 cents; SO_2 leaching, 9.3 cents. The point may be raised that by a sulphuric-acid plant the Clifton smelter could produce sulphuric acid locally at a cost not to exceed $5 per ton, including plant amortization; then the comparative costs of reagents would be as follows: H_2SO_4 leaching, 20.75 cents per ton; SO_2 leaching, 9.3 cents per ton. In comparing the results these facts must be given due consideration: Sulphuric-acid leaching was performed under more favorable conditions than SO_2 leaching on account of the extremely irregular density of pulp in the latter. The absorption of SO_2 was poor, not over 40 per cent. The authors have since developed a double-drum system at Tucson which gives an SO_2 absorption as high as 90 per cent and a higher dissolution of copper on all pulps treated. Recent results point to greater economy of reagent and to decidedly increased dissolution.

SHANNON OLD MILL TAILING.

A special run on Shannon tailing was begun in December, 1920. The composition of the tailing is indicated in Table 15, which shows their consumption of acid is rather high. It was thought at the time of the first leaching that by maintaining an excess of SO_2 in the drum at all times enough acid would be present to effect a satisfactory dissolution of copper. A review of the results indicates clearly that there is another essential condition—proper absorption of SO_2. As the acid-soluble constituents of an ore increase, the pulp density should be decreased in order to provide ample absorption medium. An alternative measure would be to increase the time of contact which would result in the utilization of absorbed SO_2 to form sulphates, thus releasing SO_2 and leaving the solution free to absorb fresh SO_2. During December, 1920, and January and February, 1921, the over-all extractions recorded were as follows:

TABLE 8.—*SO_2 leaching recoveries as recorded and corrected for defective washing of filter cake.*

Per cent Cu.	December, 1920.		January, 1921.		February, 1921.	
	Recorded.	Corrected.	Recorded.	Corrected.	Recorded.	Corrected.
Sulphide	49.00	49.00	60.34	60.34	67.80	67.80
Nonsulphide	65.40	78.33	64.00	81.36	77.71	87.80
Total	62.50	72.63	63.2	76.73	75.37	82.32

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The recorded extraction is based on the copper content of the Oliver filter-cake tailing. Detailed daily reports for these three months indicate that, because of insufficient washing, this tailing in December contained 0.11 per cent water-soluble copper; in January, 0.15 per cent; and in February, 0.09. The filter used was old and gave more or less trouble throughout the tests, but until the last few months the water-soluble copper in the filter cake was readily maintained at 0.01 per cent Cu. It is reasonable to assume that under proper operating conditions in a well-equipped plant a filter cake containing only 0.01 per cent could be maintained. On this assumption a corrected column is added for these three months to indicate what would be the non-sulphide recovery with proper washing.

A peculiar condition developed within the leaching drum toward the end of treatment of the Shannon tailings. Soluble lime precipitated as $CaSO_4$ and formed a solid incrustation or scale on the interior woodwork, partly closing the holes in the vertical disk baffles. For ores of this kind the openings in the disks might well be made larger. Accumulations of scale could be removed periodically through the squirrel cage. Should it be desirable to remove the scale without entering the drum this may be done in the following manner: Sodium bicarbonate, when heated by steam, will react with calcium sulphate, leaving a soft precipitate or coating of calcium carbonate, according to the following equations:

$$4\ NaHCO_3+CaSO_4=CaH_2(CO_3)_2+Na_2CO_3+NaSO_4+CO_2+H_2O$$
$$4\ NaHCO_3+CaSO_4=CaCO_3+NaCO_3+Na_2SO_4+2CO_2+2H_2O.$$

The calcium carbonate may be removed by flushing with water; or, should part of the incrustation after changing to carbonate continue to adhere firmly to the wood, it can be dissolved quite readily with dilute hydrochloric acid. This procedure proved satisfactory for removing very hard incrustations. Undoubtedly the scale had much to do with the poor utilization of gas in the drum.

Table 9 shows the total percentage of each of the acid-soluble constituents of tailings, and the percentage of each constituent found to be soluble in varying strengths of sulphuric acid. The method of testing used (the 3 per cent solution excepted) was to mix the ore with solution, bring to the boiling point, and boil for five minutes. This statement applies to the tests ranging from 5 per cent strength to 50 per cent strength. In the case of the 3 per cent solution the procedure was to roll cold in a bottle for 24 hours. The results clearly show that dissolution of all the acid-soluble constituents varies directly as the strength of the acid, and that there is a selective action in favor of copper, especially with low acid concentrations and short contact.

TABLE 9.—*Solubility table, Shannon old mill tailings.*

	Total Cu, per cent.	Fe, per cent.	SiO_2, per cent.	Al_2O_3, per cent.	S, per cent.	CaO, per cent.	MgO, per cent.
Partial analysis of leaching Heads	1.05	5.1	62.4	10.6	0.8	2.6	2.9
Per cent of each constituent dissolved in following strengths of solution:							
3 per cent H_2SO_4	48.8	21.2	.11	3.2	....	20.0	11.9
5 per cent H_2SO_4	61.9	26.7	.16	4.5	8.1	24.0	20.4
7.5 per cent H_2SO_4	67.8	32.9	.16	5.9	32.1	27.0	26.7
10 per cent H_2SO_4	68.0	38.9	.19	7.7	32.9	28.0	29.5
25 per cent H_2SO_4	72.6	69.0	.20	17.6	34.8	33.5	43.2
50 per cent H_2SO_4	80.9	94.0	.20	19.0	36.2	33.0	45.0

In a number of subsequent tabulations dealing entirely with SO_2 leaching results, a column is added headed "Acid loss in pounds 100 per cent H_2SO_4 per ton of ore." This "acid loss" must not be regarded as indicating the consumption of SO_2; it serves merely to identify the ore tested in terms of a generally known and accepted measure. Usually the SO_2 consumption will be much less because the concentration of the SO_2 in the leach is low, the time of contact is short, and the resulting selective action favors copper minerals.

During January, 1921, for each ton of Shannon old-mill tailing 181 pounds of concentrate containing 34.5 per cent sulphur was roasted; 80 per cent of this sulphur was expelled as SO_2 and 66 per cent of the SO_2 was absorbed in the drum. In terms of sulphur and copper this means 3.12 pounds of sulphur were consumed per pound of Cu recovered, with an 81.36 per cent extraction of the soluble copper. Although no mill run on Shannon tailings was made during the work with sulphuric-acid leaching plant, laboratory tests indicate that a 24-hour cold leach with 3 per cent sulphuric acid will recover 78.8 per cent of the soluble copper with a consumption of 95.4 pounds of 100 per cent sulphuric acid, or 31.1 pounds of sulphur, equivalent to 3.03 pounds of sulphur consumed per pound of Cu recovered, with a 78.8 per cent extraction of the soluble copper. The comparison may then be stated as follows:

40-minute hot SO_2 leach=3.12 pounds S per pound Cu=81.36 per cent extraction.

24-hour cold H_2SO_4 leach=3.03 pounds S per pound Cu=78.8 per cent extraction.

Theoretically 1 pound Cu requires 0.51 pound of sulphur; the excess sulphur is consumed by one or more of the acid-consuming minerals, such as soluble iron, lime, magnesia, and aluminum. It has been demonstrated that a leach with a low percentage of acid will consume a smaller proportion of gangue minerals, yield a cleaner pregnant solution, and necessitate correspondingly less discard solution to reject "built-up" impurities. SO_2 leaching is necessarily done with a low percentage of acid, since absorption of more than 1.5 per cent SO_2 is not practicable under the operating conditions.

TABLE 10.—*SO_2 leaching results, by periods, obtained on Shannon old mill tailings.*

Products.	Shannon old mill tailings.						
	SO_2 leaching results, month of—			Weekly analytical results, month of February.			
	December, 1920. (1)	January, 1921. (2)	February, 1921. (3)	1 to 7. (4)	8 to 14. (5)	15 to 21. (6)	22 to 28. (7)
Feed to plant:							
Weight treated, dry tons	631	758	378.86	95.40	115.32	71.22	96.92
Assay per cent total Cu	.96	1.08	1.09	1.06	1.05	1.12	1.14
Assay per cent acid-soluble Cu	.78	.81	.82	.81	.79	.86	.84
Assay per cent sulphde Cu	.18	.27	.27	.25	.26	.26	.30
SO_2 drum feed:							
Assay per cent total Cu	.71	.72	.70	.69	.72	.69	.68
Assay per cent acid-soluble Cu	.64	.64	.63	.62	.65	.62	.60
Assay per cent sulphide Cu	.07	.08	.07	.07	.07	.07	.08
Pulp temperature, °C	5	7	9	7	8	8	12
Drum discharge:							
Pulp temperature, °C	35	41	46	45	47	44	47
Per cent SO_2 in pulp	1.4	1.09	.47	.42	.57	.43	.43
Blowing-tank discharge:							
SO_2 in pulp, per cent	.25	.23	.05	.04	.06	.06	.05
Pulp ratio	.98:1	.99:1	1.18:1	1.18:1	1.16:1	1.21:1	1.19:1
Cu in solution, per cent	.38	.39	.44	.46	.47	.42	.41
Cu in washed residue, per cent	.30	.31	.22	.20	.19	.24	.26
Roaster data:							
Weight dry concentrates fed	66,600	111,250	171,300	31,050	47,650	41,700	50,900
Assay per cent S. in concentrates	34.34	33.5	32.6	32.6	32.6	32.6	32.6
Temperature of roaster gases, °F	552	601	587	587	....	....	....
Assay per cent S. in calcine	6.32	6.60	6.87	8.21	6.59	6.74	6.08
SO_2 in gas to drum, per cent	4.34	4.71	5.50	4.80	5.58	5.75	5.79
SO_2 in gas from drum, per cent	1.55	1.57	2.55	1.91	2.50	2.88	2.95
Absorption of SO_2, per cent	64.29	66.67	53.84	60.21	55.20	49.91	49.05
Flotation feed:							
Weight treated, dry tons	435	528.61	291.42	68.30	80.91	58.97	83.24
Assay per cent total Cu	.95	1.00	1.02	1.04	1.01	1.03	1.01
Assay per cent undis. acid-sol. Cu	.78	.78	.78	.79	.78	.78	.76
Assay per cent sulphide Cu	.17	.22	.24	.25	.23	.25	.25
Flotation tailing:							
Assay per cent total Cu	.71	.72	.70	.70	.69	.67	.72
Assay per cent undis. acid-sol. Cu	.64	.64	.63	.64	.62	.61	.64
Assay per cent sulphide Cu	.08	.07	.07	.06	.07	.06	.08
Tons into one	27.5	33	30	28	33	21	36
Flotation concentrate:							
Weight produced, dry tons	15.83	16.12	9.89	2.45	2.45	2.83	2.30
Assay per cent total Cu	7.04	10.22	10.13	10.17	11.27	8.18	11.22
Assay per cent acid-sol. Cu	2.09	2.11	2.09	2.14	2.22	1.93	2.09
Assay per cent sulphide Cu	4.95	8.11	8.04	8.03	9.05	6.25	9.13
Recovery of total Cu, per cent	26.97	31.17	33.70	35.11	33.75	38.07	30.68
Recovery of sulphide Cu, per cent	53.81	68.78	71.46	76.57	70.11	76.74	68.60
Oliver filter cake:							
Assay per cent total Cu	.37	.38	.26	.23	.23	.26	.31
Assay per cent undis. acid-sol. Cu	.17	.14	.09	.07	.07	.08	.13
Assay per cent water-sol. Cu	.11	.15	.09	.08	.08	.09	.09
Assay per cent sulphide Cu	.09	.09	.08	.08	.08	.09	.09
Extraction (waste tails):							
Per cent of total Cu recovered	62.5	63.2	75.37	78.68	77.92	75.97	70.16
Per cent of sulphide Cu recovered	49	60.3	67.80	69.38	66.27	65.33	64.99
Per cent of acid-sol. Cu recovered	65.4	64	77.71	81.23	81.35	79.25	71.85
Over-all extraction (based on 0.01 per cent):							
Water-sol. Cu in Oliver filter cake—							
Per cent total Cu	72.63	76.73	82.35	84.34	84.76	83.93	80.70
Per cent sulphide Cu	49	60.34	67.80	69.38	66.27	65.33	64.99
Per cent nonsulphide Cu	78.33	81.36	87.80	90.12	89.87	89.53	83.33

Table 10 gives complete operating data averaged for each of the three months' operation on Shannon tailing, and a weekly analysis of the last month. Steady improvement in dissolution of copper is indicated. The showing in the weekly analysis for February (columns 4–7) is very creditable for a feed averaging slightly under 1 per cent total copper and 0.60 per cent nonsulphide copper. The progressive decline in utilization of SO_2 during February is doubtless due to the accumulation of scale (see p. 51).

Before the tests originally planned were completed, work at the Clifton experimental plant was suspended because of the general retrenchment forced on the copper companies by industrial conditions. During the interim, a laboratory-scale investigation was conducted at Tucson which will result in higher recovery of copper and better utilization of SO_2 when the Clifton tests are resumed. The Tucson investigation was carried on with reference to the three distinct problems encountered: Resistant silicates at Miami; a gangue high in lime and low in copper at Clifton; and the combination of resistant silicates, high acid-soluble gangue and high copper content in ores from the Walker River Copper Co., Yerington, Nev.

TUCSON EXPERIMENTAL WORK, 1921.

The Miami experiment fully demonstrated on a 100-ton scale the mechanical and metallurgical feasibility of SO_2 leaching with hot roaster gases. It also proved conclusively that the sample on which the original Tucson results were obtained was not representative, that a large proportion of the soluble copper in the Miami mixed ore occurs as a dilute solid solution of copper silicate in silica and that this silicate is very difficultly soluble in SO_2 and more readily soluble in sulphuric acid. It was evident that more laboratory work would be necessary to solve the problem of dissolution of these refractory silicates. With the cessation of cooperative work at Miami and Clifton, the attention of the Tucson laboratory was centered on this problem. The need for a pilot apparatus in which satisfactory laboratory tests could be made on a 10 to 50 pound scale had long been evident. At first thought it seemed that to reproduce the drum on a laboratory scale would be tantamount to going into the toy-making business. Various combinations embodying Pachuca tanks and absorption towers were tried out and abandoned, as the results obtained were neither satisfactory nor representative. Evidently a laboratory size drum was the only way out.

APPARATUS.

Accordingly an apparatus was finally evolved to reproduce as nearly as possible operating conditions in the drum. This apparatus has given continuous and satisfactory service for 12 months; it is shown in outline in Plate V. The two drums are identical, and may be operated singly or in series. The admission of air and SO_2 is under perfect control. To give the desired leaching temperature the mixture of air and SO_2 is preheated by passing through iron pipes externally heated by electric current. Limitations of small-scale construction prevented an exact reproduction of all details of the interior of the drum; for instance, in order to have the necessary longitudinal baffles to effect proper spraying and splashing, the openings in the vertical disk baffle had to be made smaller in order to have any vertical disk left. These small openings clog proportionately more easily than the larger openings in the full-size drum. As a consequence, it became necessary to run tests in the pilot drum with a pulp density of 4:1. The time of travel through this 9-inch by 36-inch drum is from 30 to 40 minutes. Comparing the results obtained in a single-pilot drum, reproducing the operating conditions of the Miami and Clifton drums and using the identical feed, has satisfied the authors that the pilot plant so closely approximates the work of the large plants that the results may be safely accepted as indicating what may be expected in actual commercial operations. The authors have also conclusively determined by comparative tests that the use of ordinary roaster gases does not introduce any complications that might produce results differing from those obtained by using pure gas.

In both the Miami and the Clifton experimental plants the leaching solutions after precipitation were run to waste. Special provision would have been required to reclaim these solutions for reuse in the leaching circuit; the easier and cheaper course with regard to test-plant construction was to send them to the mill pond. Generally, it is practicable to recover 60 per cent of the water or solution from a milling or leaching operation. An ore containing 1 per cent soluble copper, leached at 1:1 pulp density and the copper precipitated on iron, would yield a waste solution containing 0.25 per cent Fe, as $FeSO_4$. By reclaiming and using 50 per cent of the waste solution, the leaching solutions would soon build up to 0.5 per cent Fe. Had this practice been followed in the operation of the Miami drum, the discoveries made with the Tucson pilot drum would doubtless have been anticipated by two years and the Miami experiment would have been an unqualified success.

Observation of certain leaching effects in the Tucson pilot drum led to special research, with a view to utilizing the drum as a convenient apparatus for making weak sulphuric acid. By special but simple control it proved quite practicable rapidly to oxidize ferrous sulphate, in the presence of SO_2, to ferric sulphate; this ferric sulphate in turn reacts with SO_2 to form ferrous sulphate and sulphuric acid. Therefore the operation of the pilot drum was controlled to include this reaction, with the result that the most resistant silicates readily decompose during passage through a short drum (36 inches) in which the pulp is retained for 30 to 40 minutes. A large number of tests were made on a wide range of ores, including ores that have soluble lime and other strongly acid-destroying gangue minerals. In all tests the copper content of the tailing was very low.

TABLE 11.—*Comparison of dissolution of nonsulphide copper in single and double drum leaching without and with addition of 0.5 per cent Fe (as $FeSO_4$).*[a]

Name.	Nature of ore.	Test No.	Feed assay, nonsulphide Cu, per cent.	Single drum.				Double drum.			
				Without Fe.		0.5 per cent Fe added.		Without Fe.		0.5 per cent Fe added.	
				Tailing, per cent Cu.	Extraction, per cent.	Tailing, per cent Cu.	Extraction, per cent.	Tailing, per cent Cu.	Extraction, per cent.	Tailing, per cent Cu.	Extraction, per cent.
			(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Shannon ore, Clifton, Ariz.	Low copper; high acid-soluble lime gangue, 150 pounds acid consumed per ton.	1	0.60	0.174	71.0	0.136	77.3	0.146	75.0	0.052	91.3
		2	.60	.178	70.2	.123	79.5	.164	72.0	.046	92.3
Walker River ore, Yerington, Nev.	High copper; resistant silicates, also high acid-soluble lime and iron, 170 pounds acid consumed per ton.	3	2.27	.739	67.4	.466	79.5	.404	82.2	.077	96.6
		4	2.27	.788	65.3	.458	79.8	.391	82.8	.075	96.7
Miami ore, Miami, Ariz.	Resistant copper silicates, 64 pounds acid consumed per ton.	5	.52	.146	71.0	.050	89.8	.125	75.0	.030	94.2
		6	.74	.096	87.0	.036	95.2	.080	89.2	.024	96.7
		7	.94	.130	84.1	.041	95.6	.108	88.5	.030	96.8

[a] Feed and tailing assays include nonsulphide copper only.

COMPARISON OF SINGLE AND DOUBLE DRUMS.

Table 11 compares single-drum and double-drum work, and also compares leaching without and with Fe in solution. Tests 5, 6, and 7 on resistant Miami silicates indicate (columns 3 and 7) that recovery is increased 4 per cent for two grades of ore and 2 per cent for the third grade. The beneficial effect of Fe is noticeable in the single-drum treatment (column 5), especially if the tailing assay is considered. The double drum with iron shows an increase over the single drum with iron; the increase is hardly sufficient to warrant a double-drum installation for Miami silicates. The main advantage of a double-drum installation for this ore would lie in raising SO_2 absorption from 60 per cent, obtained in single drum, to 90 per cent. In tests 3 and 4 on an ore containing considerable acid-consuming lime and iron but relatively high in copper, much of it in the form of difficultly soluble silicate, the double drum decidedly increases copper dissolution, but a double-drum treatment with iron is needed to get a good tailing. Tests 3 and 4 are duplicate tests on the same ore.

Tests 1 and 2 (duplicates on a very low-grade ore with heavy acid-consuming gangue differ from tests 3 and 4 only in that the double drum without iron does not show much improvement over the single drum without iron. It takes the double drum with iron to make a satisfactory tailing.

Double-drum tests generally give better dissolution of copper and much higher utilization of SO_2 than single-drum tests. The most easily soluble constituents of the ore are brought in contact in the first drum with the partly spent, cold gas from the second drum. The partly leached ore then comes in contact with a large excess of hot SO_2 gas in the second drum under the best conditions for dissolution of any refractory copper minerals.

TABLE 12.—*Capacity tests, single drum versus double drum (operating in series).*

Name.	Nature of ore.	Test No.	Feed assay, nonsulphide Cu, per cent.	Single-drum leaching results.					
				Rate of feed in grams per hour.	Per cent SO_2 utilization.	Discharge pulp.		Tailing assay, nonsulphide Cu, per cent.	Apparent extraction, per cent.
						Free H_2SO_4.	Ferric iron.		
Miami ore	Regular mixed ore, resistant copper silicate.	1	0.74	2,000	42	0.06	0.05	0.025	96.0
Walker River ore, Yerington, Nev.	Resistant copper silicate, high acid-soluble gangue, high soluble copper content.	2	2.61 2.61	1,000 2,000	42 63	.40 .11	.18 .20	.10 .39	96.1 85.0
Shannon tailing	High acid-soluble gangue, low soluble copper content.	3	.60 .60	1,000 2,000	60 65	.10 .07	.05 .05	.052 .12	91.3 79.5
Clifton tailing	Low acid-soluble gangue, higher soluble copper content.	4	.90 .90	1,000 2,000	39 65	.50 .12	.05 .05	.02 .06	98.0 93.3

Name.	Nature of ore.	Test No.	Double-drum leaching results (drums operated in series on double feed to first drum).					
			Rate of feed in grams per hour.	Per cent SO_2 utilization.	Discharge pulp.		Tailing assay, nonsulphide Cu, per cent.	Apparent extraction, per cent.
					Free H_2SO_4.	Ferric iron.		
Miami ore	Regular mixed ore, resistant copper silicate.	1	4,000	85	0.05	0.05	0.02	97.3
Walker River ore, Yerington, Nev.	Resistant copper silicate, high acid-soluble gangue, high soluble copper content.	2	2,000 4,000	94 94	.44 .06	.19 .20	.075 .38	97.1 85.4
Shannon tailing	High acid-soluble gangue, low soluble copper content.	3	2,000 4,000	87.5 90.4	.40 .08	.05 .05	.046 .119	92.3 80.2
Clifton tailing	Low acid-soluble gangue, higher soluble copper content.	4	2,000 4,000	69 98	.60 .33	.06 .06	.01 .04	99.0 95.5

In order to determine whether the increased dissolution of these minerals and the increased utilization of SO_2 were obtained at the expense of decreased capacity per drum, the tests reported in Table 12 were made. The rate of feed established on regular Miami mixed ore, 2,000 grams per hour for a single drum, was adopted as the standard for comparison. Comparative tests were made on 1,000 grams per hour, single drum, and 2,000 grams per hour, double drum (in series); also on 2,000 grams per hour, single drum, and 4,000 grams per hour, double drum (in series). The results showed that the dissolution of copper is slightly higher with the double drum (in series) at the same capacity per drum, and the better utilization of SO_2 is marked.

DETERMINATION OF EXTRACTION.

Analytical methods are fully discussed elsewhere in this bulletin. Three points connected with methods used to determine the extractions reported in the various tabulations are mentioned here because they have the effect of indicating slightly lower apparent extractions than is actually obtained.

Apparent extraction.—Apparent extraction is determined from the equation:

$$\frac{\text{Feed assay}-\text{tailing assay}}{\text{Feed assay}}=\text{Per cent apparent extraction.}$$

As the leach dissolves both the acid-soluble copper and a varying quantity of acid-soluble gangue minerals, the bulk of the tailing is appreciably less than the bulk of original feed, and the apparent extraction reported is slightly lower than the actual extraction would be.

Oxidation of samples.—Pulps of all classes of ores show more or less progressive oxidation of sulphides during washing and drying after discharge from the drum. Consequently, the nonsulphide copper reported in the tailing is always slightly high. This tendency to oxidize, which is more pronounced in some ores than in others. may vary from 0.01 to 0.05 per cent for the ores under discussion, and should be considered in judging leaching results, particularly the results on ores containing upward of 1 per cent copper in the form of secondary sulphides. In many tests an appreciable portion of the nonsulphide copper reported in the leaching tail ostensibly as undissolved acid-soluble copper, is really attributable to progressive oxidation after leaching.

Percentage of extraction.—For low-grade ores the extraction percentage may give an erroneous impression; the tailing assay is the only correct index to the efficacy of the treatment. This point is clearly brought out in Table 11, columns 8 and 9. Tests 5 and 7 show a difference of 2.6 in per cent extraction but the two ores have the same tailing assay.

COUNTERCURRENT VS. CONCURRENT LEACHING.

The suggestion has been made that as heat seems to be an important factor in obtaining quick and complete leaching, the leaching practice might be improved by utilizing the heat of the hot gas throughout the entire leach instead of merely toward the end, this to be done by substituting concurrent for countercurrent leaching.

TABLE 13.—*Comparative results, countercurrent vs. concurrent leaching, single-drum tests.*[a]

Name.	Nature of ore.	Test No.	Feed assay, nonsulphide Cu, per cent.	Countercurrent leaching—Gas admitted countercurrent to pulp.				
				Ingoing gas, SO_2 per cent by volume.	Outgoing gas, SO_2 per cent by volume.	Utilization total SO_2 supplied, per cent.	Tailing assay, nonsulphide Cu, per cent.	Apparent extraction, per cent.
			(1)	(2)	(3)	(4)	(5)	(6)
Shannon ore, Clifton, Ariz.	Low in copper content, high in acid-soluble lime gangue; acid consumption per ton 150 pounds.	1	0.60	4.8	0.7	85.4	0.123	79.5
Walker River ore, Yerington, Nev.	High copper content, resistant silicates; also high acid-soluble lime and iron; acid consumption per ton 170 pounds.	2	2.61	4.8	1.75	63.0	.390	85.0
Miami ore, Miami, Ariz.	Most resistant silicate ore in Miami ore body, differing materially from ores reported in tests 5, 6, and 7, Table 11; acid consumption per ton 108 pounds.	3	1.79	4.8	.6	87.0	.110	93.8

Name.	Nature of ore.	Test No.	Concurrent leaching—Gas admitted with pulp.				
			Ingoing gas, SO_2 per cent by volume.	Outgoing gas, SO_2 per cent by volume.	Utilization, total, SO_2 supplied, per cent.	Tailing assay, nonsulphide Cu, per cent.	Apparent extraction, per cent.
			(7)	(8)	(8)	(10)	(11)
Shannon ore, Clifton, Ariz.	Low in copper content, high in acid-soluble lime gangue; acid consumption per ton 150 pounds.	1	4.8	2.5	48.0	0.150	75.0
Walker River ore, Yerington, Nev.	High copper content, resistant silicates; also high acid-soluble lime and iron; acid consumption per ton 170 pounds.	2	4.8	2.7	43.0	.730	72.0
Miami ore, Miami, Ariz.	Most resistant silicate ore in Miami ore body, differing materially from ores reported in tests 5, 6, and 7, Table 11; acid consumption per ton 108 pounds.	3	4.8	2.04	57.0	.380	79.4

[a] Feed and tailing assays include nonsulphide copper only.

To settle this question, comparative single-drum leaching tests were made by both methods on three representative ores. The results as reported in Table 13 are decidedly favorable to countercurrent leaching. Both the apparent extraction on the two silicate ores and the SO_2 utilization are satisfactory in a single-drum countercurrent treatment and far from satisfactory in the concurrent treatment.

In order to determine the effect of "built-up" iron on the reuse of reclaimed solutions, a series of tests was made in the pilot drum, using one drum only, in the following manner:

Under standard operating conditions for a period of four days (30 hours) all the leached pulp was stored in crocks until it settled, when the clear solution was decanted. About 80 per cent of the solution was recovered, passed over iron for removal of copper, and reused for pulping new ore. No fresh water was added, consequently the second run was of correspondingly shorter duration—24 hours. The pulp discharged during the second run was treated like that from the first, its volume being reduced to 80 per cent of that recovered from the first operation. No fresh water was added. Each succeeding run was of shorter duration because of the progressively smaller volume of solution. The sixth or final run lasted eight hours. The results are recorded in Table 14.

TABLE 14.—*Effect of built-up iron through reuse of reclaimed leaching solutions.*

Leaching stage.	Analysis of solutions.						Per cent nonsulphide Cu.		Per cent apparent extraction.
	Entering drum.			Leaving drum.					
	Cu.	H_2SO_4.	Fe.	Cu.	H_2SO_4.	Fe.	Feed.	Tailing.	
0 New solution	None.	None.	0.50	0.24	0.45	0.05	0.74	0.026	96.4
1 First reuse	0.01	None.	.74	.23	.32	.75	.74	.022	97.0
2 Second reuse	.01	None.	.96	.22	.45	.98	.74	.028	96.2
3 Third reuse[a]	.01	.07	1.23	.20	.18	1.20	.74	.043	94.2
4 Fourth reuse[a]	.08	None.	1.48	.21	.09	1.52	.74	.050	93.2
5 Fifth reuse	.01	None.	1.70	.22	.40	1.78	.74	.026	96.4

[a] Attention is called to the relatively low extraction with third and fourth reuse solutions and the correspondingly low sulphuric acid content from the drum discharge solutions.

In order to determine the applicability of the process, representative samples were obtained from the so-called "porphyry copper" mines of the Southwest and from a number of undeveloped districts in Arizona and Nevada. These samples were carefully tested as follows: Ore crushed to 40 mesh; pulp density, 4:1; double-drum tests; leaching time, 30 to 40 minutes. Plant operated until balanced leaching conditions were established; for a new ore this adjustment sometimes required three to four days. After balanced conditions were attained, samples were taken at 30-minute intervals; not less than 10 samples to the test.

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The results indicate that all the "porphyry copper" ores should give a high extraction by leaching in a large drum. Copper ores occurring in limestone usually have a highly acid-consuming gangue. With such ores it is necessary either to increase the percentage of gas or to decrease the rate of feed according to the consumption of acid. Table 15 summarizes the average results on a number of typical ores. Table 16, a work sheet of a single test, indicates the data recorded and calculated for each test.

TABLE 15.—*Summary of SO_2 leaching tests (with addition of $FeSO_4$) in pilot drum on representative ores.*

Name.	Pulp analysis.					Per cent copper.				Per cent apparent extraction.	
	Insoluble.	Fe_2O_3 and Al_2O_3.	S.	CaO and MgO.	Acid loss 100 per cent, H_2SO_4 pounds per ton.	Drum feed, per cent Cu.		Drum tailing, per cent Cu.		Non-sulphide Cu.	Sulphide Cu.
						Non-sulphide.	Sulphide.	Non-sulphide.	Sulphide.		
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
Miami Copper Co.	92.8	2.60	0.60	0.20	64	0.74	1.03	0.02	0.66	97.3	36.0
Inspiration Cons. Copper Co.	93.7	2.62	.75	.75	118	1.14	.20	.075	.18	93.5	10.0
New Cornelia Copper Co.	85.4	7.84	2.90	Trace.	178	1.27	.59	.08	.43	94.0	27.1
Ray Cons. Copper Co.:											
Concentrating ore	85.0	6.80	2.80	.20	49	.52	1.28	.04	.87	92.0	32.0
Refractory silicate ore.	70.4	16.00	.20	.50	206	1.27	.62	.07	.50	94.5	20.0
Arizona Copper Co.:											
Shannon old tailings	79.0	10.40	.80	1.20	150	.60	.64	.05	.50	91.3	22.0
Clifton old tailings	63.4	22.20	.58	.83	64	.90	.38	.01	.25	99.0	34.0
Morenci old tailings	66.0	18.96	.72	.54	83	.58	.32	.03	.24	94.8	23.0
Chino Copper Co., N. Mex.	85.8	8.15	1.0	.50	137	1.42	1.15	.09	.74	93.7	35.6
Tyrone, N. Mex	85.4	6.40	3.9	.20	54	.57	1.63	.08	1.22	86.0	25.0
Utah Copper Co., oxidized capping	89.18	9.06	.10	.30	87	.70	.06	.04	.05	94.3	17.0
Silverbell, Ariz	43.47	33.50	2.63	1.04	234	4.45	1.87	.38	1.35	91.5	27.8
Pinto Valley, Ariz	81.70	4.82	.12	.80	210	5.29	.39	.18	.31	96.6	20.5
Walker River Copper Co., Yerington, Nev	78.60	7.40	.20	.30	170	2.27	.12	.077	.09	96.6	25.0
Electrolytic mine, Luning district, Nev	55.21	15.77	Trace.	3.00	627	2.36	.43	.26	.36	89.0	16.0
Mayflower mine, Luning district, Nev	69.36	13.16	Trace.	2.40	343	2.60	.29	.14	.24	94.7	17.2
Pilot Copper mine, Luning district, Nev	43.8	17.53	.75	.67	250	5.11	1.51	.25	1.16	95.2	23.2

These tests revealed an entirely unexpected dissolution of sulphides, which were obtained during a leaching treatment designed to dissolve nonsulphide copper, and produce a maximum of sulphuric acid and a minimum of ferric iron. In these tests the solutions discharged from the drum averaged 0.05 per cent ferric iron. The dissolution of sulphide was attributed to the ferric iron made in the regular leaching cycle. In confirmatory tests in glass cylinders the ferric iron was increased to 0.5 per cent and a dissolution of sulphides up to 75 per cent was obtained. The authors find that air, in the presence of small amounts of SO_2, causes rapid oxidation of ferrous iron to ferric iron. When more than 2 per cent SO_2 is present, the SO_2 immediately reacts with the ferric iron to form sulphuric acid and ferrous iron. As the percentage of SO_2 decreases, less ferric iron is broken up and more is available for dissolution of sulphide copper. When the SO_2 content of the gas is under 0.5 per cent, nearly all the iron is oxidized to the ferric state and apparently enough sulphuric acid is made to have an appreciable leaching effect on resistant copper silicates. This opens up an entirely new phase of SO_2 leaching which has interesting possibilities

TYPICAL DATA SHEET.

TUCSON, ARIZONA.

Date received, May 2, 1921. Sample from Miami Copper Co., Miami, Ariz.

Lab. No. 128.

Date test, May 27, 1921.

ANALYSIS.

Insol., per cent	92.8	Sulphur, per cent	0.6
Fe_2O_3, per cent	1.6	Lime (CaO), per cent	.2
Al_2O_3, per cent	1.0	Acid consumed (H_2SO_4), 64 pounds.	

Oxide Cu, 0.74 per cent; sulphide Cu, 1.03 per cent; total Cu, 1.77 per cent.

LEACHING TEST BY SULPHUR DIOXIDE PROCESS.

Double drum, with addition of 0.5 per cent Fe as ferrous sulphate.

Feed at 40-mesh at rate of 2,000 grams per hour. Pulp ratio, 4 to 1.

Volume of air plus SO_2 gas, 30 liters per minute.

Ingoing gas, 5 per cent SO_2. Outgoing gas, 2 per cent SO_2. Gas efficiency, 60 per cent.

Temperatures: Feed pulp, 26° C.; tailing pulp, 39°.; ingoing gas, 175° C.

Iron in discharge solution: 0.05 per cent ferric iron; 0.46 per cent ferrous iron.

TABLE 16.—*Results based on samples cut from tailing flow every 30 minutes.*

Sample No.	Analysis of discharge solution (per cent).		Analysis of tailing (per cent).			Apparent extraction (per cent).		
	H_2SO_4	Ferric iron.	Copper.			Copper.		
			Oxide.	Sulphide.	Total.	Oxide.	Sulphide.	Total.
1	0.17	....	0.026	0.60	....	96.5	42.0	....
2	0.15	....	0.026	0.66	....	96.5	36.0	....
3	0.20	0.05	0.022	0.72	....	97.0	30.0	....
4	0.17	....	0.022	0.68	....	97.0	34.0	....
5	0.17	....	0.014	0.64	....	98.1	38.0	....
6	0.18	....	0.014	0.62	....	98.1	40.0	....
7	0.24	0.04	0.013	0.70	....	98.3	32.0	....
8	0.27	....	0.013	0.66	....	98.3	36.0	....
9	0.25	....	0.026	0.65	....	96.5	36.8	....
10	0.30	0.06	0.026	0.67	....	96.5	35.2	....
Average per cent	....	0.05	0.02	0.66	0.68	97.3	36.0	61.0

REMARKS.

Straight SO_2 leaching test, run for dissolution of nonsulphide copper only. Apparent extraction of nonsulphide copper, 97.3 per cent, with 0.02 per cent tailing. Dissolution of 35.2 per cent of sulphide copper content is wholly incidental.

GENERAL DISCUSSION OF PROCESS.

A leaching investigation may be considered as coming under four main heads: Dissolution of metal; recovery of metal; necessary allied operations; and competing processes and utilization—that is, the economics of the problem. This paper is primarily a report covering in detail the first phase—dissolution of copper. The other three phases will be mentioned briefly.

RECOVERY OF COPPER.

The copper is recovered from sulphate solution by precipitation in one of several ways, as indicated below:

1. *Electrolytic precipitation.*—Electrolytic copper has obvious advantages as a marketable product. How far electrolytic recovery might be commercially available in connection with SO_2 leaching is a point that has received little attention, as the SO_2 leaching solutions obtained from the ordinary run of mixed ores mined in the Southwest are low in copper (0.3 to 1.25 per cent), electrolytic precipitation would require building up the copper content of the pregnant solution by reuse; this would involve pebble grinding in acid-proof ball mills and filtration in acid-proof filters.

2. *Precipitation in the pulp on iron.*—The possibility of precipitating on iron, preferably sponge iron, the copper in the pulp, subsequently recovering cement copper and any remaining sulphide by flotation and smelting the combined concentrate, has been considered in some detail under the caption "Flotation results on cement copper," page 37.

3. *Countercurrent decantation and precipitation of cement copper on sponge iron in clear pregnant solution.*

4. *Precipitation from clear solution obtained by filtration instead of decantation.*

Of methods 2, 3, and 4, method 2 is most advantageous as to plant investment, cost, and simplicity of operation. It is assumed that a recovery of 90 per cent of the precipitated copper can readily be obtained, also that the maximum recovery to be expected under the most favorable condition would hardly exceed 95 per cent. On the other hand, method 3, countercurrent decantation, has the advantage of higher recovery of the dissolved copper, at least 98 per cent recovery being assured. Against this higher recovery are the greater cost of plant and the large volume of wash water required in decantation. The

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feasibility of this method would depend largely upon the settling quality of the pulp. Some pulps settle so slowly as to preclude decantation.

Method 4, filtration, is merely suggested as a possible alternative to countercurrent decantation, for its availability depends upon finding a satisfactory acid-proof filter. One of the copper companies recently tested an ore having the following composition: Insoluble, 92.8 per cent; Fe_2O_3, 1.6 per cent; Al_2O_3, 1.0 per cent; CaO, 0.2 per cent. The pulp produced was very flocculent, and when it was leached with cold sulphuric acid the results of filtration were most disappointing. Small-scale tests of the same ore in the Tucson laboratory indicate that the filtration of hot SO_2 leaching pulps might prove to be simpler.

NECESSARY ALLIED OPERATIONS.

Under this head the principal considerations are as follows: Generation of leaching reagent; making sponge iron for precipitation of copper; filtration of hot acid pulp solutions.

GENERATION OF LEACHING REAGENT.

For the SO_2 leaching at Miami two grades of massive iron pyrite, containing, respectively, 40 per cent and 50 per cent of sulphur, were imported; they cost $8 per ton delivered at the plant. Roasted down to 2 per cent sulphur, they proved very satisfactory.

At the experimental mill of the Arizona Copper Co., local granular concentrates containing 34.5 per cent sulphur were roasted until 80 per cent of the sulphur was eliminated, yielding 552 pounds of sulphur per ton. It is estimated that the cost of producing sulphurous acid (H_2SO_3), including cost of delivering SO_2 to the drum on a reasonable scale of operations, from a concentrate that will yield 640 pounds available sulphur, will be $1.20 per ton of concentrates or 0.06 cent per pound of H_2SO_3. Table 17 gives in convenient form the sulphur requirements per pound of copper and of the other soluble minerals present; also the equivalent requirements in 100 per cent H_2SO_4, and in 60°B. acid. The sulphurous acid (100 per cent H_2SO_3) equivalent of a pound of sulphur was calculated and is reported in four parallel columns based upon varying absorption of SO_2 in the leaching drum. In single-drum installations an absorption of 50 to 60 per cent may be attained; in double-drum work the absorption ranges from 70 to 90 per cent.

Table 18 gives cost of reagent in terms of cost per pound of sulphur delivered in the form of SO_2 to the drum intake. For comparative purposes, the cost of a pound of sulphur in the form 60°B. sulphuric acid is added.

TABLE 17.—*Reagent requirements, S, H_2SO_3, H_2SO_4 per pound of different soluble elements.*

One pound of—	Sulphur.	Reagent required, pounds.					
		Sulphurous acid, 100 per cent H_2SO_3, weight based on SO_2 absorption, varying with operating conditions.				Sulphuric acid H_2SO_4.	
		50 per cent.	60 per cent.	75 per cent.	90 per cent.	100 per cent H_2SO_4.	60° B. H_2SO_4.
Soluble Cu	0.51	2.43	2.03	1.62	1.35	1.56	2.10
Soluble Fe	0.57	2.72	2.27	1.81	1.50	1.75	2.25
Soluble Al_2O_3	0.94	4.48	3.73	3.00	2.50	2.88	3.70
Soluble CaO	0.57	2.72	2.27	1.81	1.50	1.75	2.00
Soluble MgO	0.80	3.82	3.20	2.55	2.12	2.45	3.16

TABLE 18.—*Cost of one pound of S delivered as SO_2 to drum intake.*

Source	Net available sulphur content per ton, pounds.	Over-all cost per ton of material, including conversion.	Cost per pound of sulphur delivered into drum, cents.
(a) Local concentrates	600	$1.00	0.167
(b) Local pyrite ore	800	5.00	0.625
(c) Imported pyrite ore	800	9.25	1.112
(d) Native sulphur	1,600	24.00	1.500
(e) 60° B. sulphuric acid	507	10.00	2.000

This table has been compiled on the assumption that sulphur will be available from one of four sources as noted below:

(*a*) Local concentrates, such as chalcopyrite or cupriferous iron pyrite, destined for shipment to smelter, at many places are the cheapest possible source of sulphur. The actual cost of sulphur chargeable to leaching operations would obviously vary with local conditions. It is conceivable that the saving in freight charges through reduction of weight by roasting, and the saving in smelting cost, should the practice at a particular smelter include a charge for roasting, might offset the total cost of roasting and handling at the leaching plant. On the other hand, with a local smelter available, designed for the treatment of concentrates and dependent upon the sulphur content to furnish fuel for the charge, the cost of leaching reagent from the same source would be the full cost of handling at the leaching plant plus the smelter penalty for sulphur deficiency in roasted concentrates. The possibility of so controlling the roast as to convert the copper in the concentrates into water-soluble or acid-soluble copper will, of course, receive due consideration in each specific case. Generally speaking, the calcine would be considered a desirable smelting product, but its desirability would be affected by such considerations as precious metal content, copper content, and distance to smelter. If the calcine carries no gold and silver, if its copper content is relatively low and the haul to smelter is long, and if the concentrates contain no elements, such as arsenic and antimony that would be troublesome in roasting and leaching, then it might be well worth while to consider the roasting and leaching of the concentrates, always remembering that only large-scale experimentation will give dependable roasting data. For estimating purposes a concentrate is assumed to yield 30 per cent available sulphur at an over-all cost of $1 per ton of concentrates for delivery of 600 pounds of sulphur into the drum in the form of SO_2.

(*b*) Probably the commonest source of sulphur will be local pyrite or imported massive pyrite. The choice may be between a local pyrite containing perhaps 20 per cent suphur and a high-grade imported pyrite running 40 to perhaps 50 per cent sulphur. Arriving at a decision would be largely a matter of figuring balances. In the present discussion no account can be taken of possible recovery of precious metal or of copper on the one hand, or of possible utilization of any iron in the calcine on the other hand. All pyrite ores should be crushed to 4–6 mesh, a satisfactory fineness both for roasting and for subsequent deoxidation. Local pyrite is assumed to contain 40 per cent available sulphur and to cost $3.75 per ton delivered at the leaching plant. To this, $1.25 must be added per ton to cover crushing, handling, roasting, etc., making an over-all cost of $5 for delivering 800 pounds of sulphur in the form of SO_2 into the leaching drum.

(c) Large deposits of massive pyrite, low in copper and other valuable minerals, carrying upward of 40 per cent sulphur, have been opened up in several localities. These deposits are geographically distributed so as to make iron pyrite rather generally available at $6 to $8 per ton delivered at the principal copper-leaching plants. For estimating purposes, it is assumed that imported massive pyrite containing 800 pounds available sulphur will cost $8 per ton delivered at the leaching plant and that the over-all cost of delivering 800 pounds of sulphur into leaching drum will be $9.25.

(*d*) Very few localities where sulphur in one of the three forms mentioned above could not be obtained locally or within a reasonable radius are known to the authors. The most expensive form, but also the most concentrated form of sulphur, is native sulphur, which is occasionally available in the West in competition with other forms. There are no metallurgical objections whatever to using native sulphur, and under certain conditions it might be the cheapest source. It may be quite efficiently used in burners of simple construction.[14] Impure sulphur containing 80 per cent available sulphur is assumed to be available at a cost of $24 for delivering 1,600 pounds of sulphur as SO_2 into the leaching drum.

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[14] For descriptions of sulphur burner and pyrite roaster, see Wells, A. E., and Fogg, D. E., Manufacture of sulphuric acid in the United States, Bull. 184, Bureau of Mines, 1920.

(*e*) For purposes of comparison the cost per pound of sulphur contained in 60°B. sulphuric acid at $10 per ton delivered at mill is added.

MAKING SPONGE IRON FOR PRECIPITATION OF COPPER.

One associates iron precipitation with SO_2 leaching as naturally as one associates electrolytic recovery of copper with sulphuric-acid leaching. And yet, this may in effect be placing an undeserved limitation upon the process. The writers have always regarded the successful manufacture of sponge iron as a vital part of the process, largely because it offered a complete use of both the iron and the sulphur content of sulphides used as a source of SO_2; furthermore, it offered an alternative to smelting for the recovery of the copper in these sulphides. This copper is metallized more easily than the iron, and may be recovered in various ways; the method chosen would depend partly upon which method of precipitation and recovery of cement copper is adopted. Experimental work in the deoxidation or metallization of iron in calcines from pyrite roasting is being carried on at the Southwest experiment station.

COMPETING PROCESSES.

On pages 12 and 13 brief mention was made of two possible and attractive processes—all-flotation, and roasting-leaching—designed to recover the entire copper content of mixed ores. Both should be considered as possible future competitors of a flotation and SO_2 leaching process. The only demonstrated and standardized process that can compete with SO_2 leaching of the nonsulphide copper in mixed ores is sulphuric-acid leaching. For the recovery of total copper in wholly oxidized ores in which sulphide copper, if present at all, exists in negligible quantity, sulphuric-acid leaching has certain undeniable advantages. By comparatively coarse crushing, 3-mesh, percolation difficulties can be minimized and a relatively small volume of reagent can effect a good dissolution of copper; 60 to 80 per cent of the dissolved copper can be recovered by electrolysis and the remainder by precipitation on iron. The plant investment is high, and the cost of power is a most important factor. When mixed ore that must be ground fine enough to liberate the sulphides is to be treated, one distinct advantage of sulphuric-acid leaching disappears, and a distinct advantage of SO_2 leaching in the drum comes to the front: It is possible to prefloat sulphides and to obtain perfect contact between pulp and leaching reagent in the drum regardless of the quantity and fineness of the slimes.

ADVANTAGES OF SO_2 LEACHING.

Summed up, the advantages of leaching with SO_2 are as follows: The plant is compact and not expensive; there are no installation difficulties; power requirements are light. Operation is simple and easily controlled; there are no delicate adjustments or critical points. Percolation difficulties common to leaching are entirely avoided. Perfect contact is assured between the finest ore particles and the reagent; thus there is excellent utilization of the reagent, which is very cheap. In consequence the process may be extended to ores with so much acid-soluble gangue that they could be treated at a profit by ordinary sulphuric-acid leaching. The process is as applicable on a relatively small as on a large scale, and small-scale operation does not necessitate an undue increase in operating cost.

MECHANICAL FEATURES OF PLANT.

POSITION OF BLOWER.

In the Miami installation the blower that delivers the hot gas to the drum is placed between the roasting furnace and the drum because, when so placed, the blower handles only hot SO_2 gas, which does not corrode iron. An objection to this arrangement is the difficulty of maintaining a gas-tight seal at both ends of the drum. If the blower were placed at the discharge end of the drum and was wholly exhausting, as has been suggested, the difficulty at the seals would be eliminated, for the effect of small air leaks into the drum at the seals would be negligible. A blower so placed would have to resist the corrosive action of condensed vapors from solutions containing ferric sulphate, copper sulphate, and free acid, hence brass, bronze, and the various forms of so-called noncorroding iron will not answer. Rather than experiment with the only remaining possibilities—antimonial lead or hardwood—the blower was placed as indicated. Since then the New Cornelia Copper Co. has demonstrated that antimonial lead can be used successfully. A standard 54-inch Buffalo blower, having the steel parts entirely covered with sheets of antimonial lead, pressed into shape and all joints burned, is used by this company in very similar service and gives entire satisfaction. It handles 6,000 cubic feet per minute of cool, moist SO_2 gas, containing some SO_3, drawing the gas from one set of towers and forcing it into another set.

INTERIOR OF DRUM.

Persons watching the operation of the process have suggested that there would be much abrasion of the interior of the drum, which consequently might be short lived. Careful examination of the interior woodwork of the Miami drum after a year's use discloses no wear. The original square corners and tight joints are everywhere in evidence. The indications are that the life of such a drum in constant operation would equal the general life of a milling plant.

CAPACITY OF LEACHING DRUM.

The long axis of the drum is horizontal, and the flow of pulp through the drum is established by the constantly incoming feed. When the drum starts, the pulp enters the first compartment and progressively passes through the succeeding compartments to the end compartment; if the discharge from this compartment is free, the rate of discharge soon becomes practically equivalent to the rate of feed. For the purpose of this discussion the pulp may be regarded as moving through the drum a segment (a compartment full) at a time, and at each revolution the volume discharged from the end compartment equals the volume fed into the first compartment. The actual volume or weight of material in the drum will vary for the same capacity, depending upon whether the end compartment discharges freely or whether the discharge level has been raised. Reference to Figure 9 will make this clear. If A represents the total volume of pulp in any compartment or segment of the drum after the pulp has found its level, a–a under condition of free discharge from the end compartment, then an incoming volume equal to A will be required to move the volume A one segment at a time to the end compartment and out of the drum. If now the end compartment is blocked as shown at M in Plate II and the discharging level is raised to b–b, then the pulp in each segment after continuous discharge has been established will be represented by B, which for present purpose is assumed to equal $2A$· Yet the volume of incoming pulp remaining A, the volume of the discharge must remain A. Moreover, the entering volume A will displace in each compartment its equivalent vol-

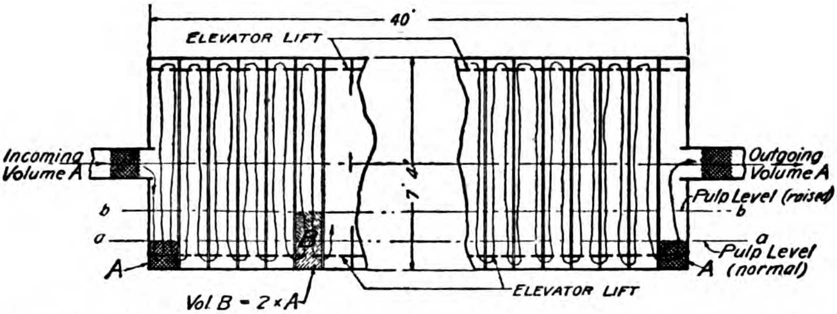

FIGURE 9.—Movement of pulp in drum and effect on drum capacity and duration of leach.

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ume A, which is only one-half of B. Obviously under these conditions the pulp remains in the drum twice as long, though the output of the drum and the speed of rotation remain unchanged. Therefore the actual volume of pulp in the drum may vary greatly for the same treatment tonnage, yet this variation in volume has no direct bearing on the tonnage treated. It has, however, an indirect bearing on the capacity of the drum, for the entire content of the drum must be agitated properly, and this is impracticable if the drum is overloaded. The lifters have a maximum capacity beyond which the entire charge will not be elevated, spilled, and sprayed at each revolution. Therefore there is a point beyond which a drum of a particular size would be overloaded. Present indications point to a capacity much larger than was assumed in the first design.

Careful observations during the operation of the Miami drum showed that the rate of flow of the gas is 3 to 6 inches per second, or 15 to 30 times the rate of the countercurrent flow of the pulp. A given volume of gas remains in any particular vertical compartment two to four seconds, but the pulp remains in a compartment about one minute, and during that time it is lifted and splashed 9 times with the drum running at 9 revolutions per minute. Assuming 45 minutes as the time necessary for pulp to pass through the Miami drum, the quantity of pulp in the drum, with free end-compartment discharge, is equivalent to a 45-minute ore feed. The load in the drum running at 100-ton daily capacity would then be $\frac{100}{24} \times \frac{45}{60} = 3\frac{1}{8}$ tons of dry ore. At a density of $1\frac{1}{2}:1$ the weight of pulp would be $7\frac{13}{16}$ tons; at a density of 1:1 it would be $6\frac{1}{4}$ tons. Thus the actual weight of dry ore in the drum corresponds very closely to the rate of feed in tons per hour multiplied by the estimated or observed time (in hours) required for complete passage through the drum. The speed of rotation has no direct bearing on capacity, but does have a direct bearing on pulp agitation, on contact between ore particle and reagent, and on gas absorption. Hence speed has an important indirect bearing on capacity. In fact, capacity is determined, first, by so regulating the speed as to obtain the showering effect that produces maximum absorption of SO_2 and maximum opportunity for contact between ore particles and reagent; and, second, by feeding into the drum all that it will handle under the best operating conditions.

An important operating requirement is proper pulp temperature. A fixed number of heat units will raise a fixed volume of pulp to a certain temperature whether the density be 4:1 or 1:1; therefore, pulp density is a controlling factor in drum capacity measured in terms of dry ore treated.

The number, size, and spacing of the horizontal baffles have an important bearing on good contact and absorption, and therefore on capacity. Properly spaced, these baffles convert the falling pulp into solid sheets of very thin spray along the entire length of the drum. The openings in the vertical disk baffles are placed directly over the longitudinal baffles both on account of convenience in construction and in order to direct the gas into the spray at each baffle. The combined area of these openings should equal or exceed the area of the pipes that convey the gas to the drum. In treating high acid-consuming ores a larger volume of gas is used per ton and the aggregate area of the openings must be correspondingly larger than in treating normal ores. In fact, for limy ores the size and spacing of these holes should be designed for the maximum openings possible without weakening the disk.

When the original Tucson installation was planned very little useful information bearing on SO_2 leaching could be found. Wells[15] records experiments on absorption of SO_2 in water which indicate that a tower with a gross volume of 20 cubic feet containing wooden block fillers that reduce the net volume by at least one-third would produce in 24 hours 10 tons of solution containing 0.5 per cent SO_2. Assuming this to be correct and assuming further that the average leaching ore consumes 100 pounds of acid per ton, it was reasonable to expect that a 4 by 16 foot drum having 200 cubic feet gross capacity would leach at least 10 tons per 24-hour day. Experiments made at Tucson on Miami ores indicated a much larger capacity; in fact, very satisfactory dissolution of copper was obtained by running at the rate of 30 tons per 24-hour day. It was assumed that 15 tons per 24-hour day for this drum would be a safe basis in designing the Miami 100-ton drum. The reason for making the drum 7 feet 4 inches inside diameter, as has been stated, was the possibility of using on-hand material. Based on the figure assumed for cubic contents, the proper length for a 100-ton drum of this diameter should be 30 feet. Further, to be safe, the drum was made 40 feet long. Careful study of operating results indicates that the additional 10 feet did no useful work whatever and that a length of 30 feet would have answered the purpose.

This drum easily leached 125 tons a day. As this was the maximum capacity of the crushing plant, it was impossible to make drum-capacity tests during regular operation. The leaching plant was closed down before arrangements could be made to test capacity by diverting pulp from other sources. The drum designed for the Arizona Copper Co.'s plant, at Clifton, intended to have a 25-ton capacity, was 5 by 20 feet, with a theoretical capacity of 29 tons.

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[15] Wells, A. E., Wet Thiogen process for recovering sulphur from sulphur dioxide in smelter gases; a critical study: Bull. 133, Bureau of Mines. 1917, p. 11.

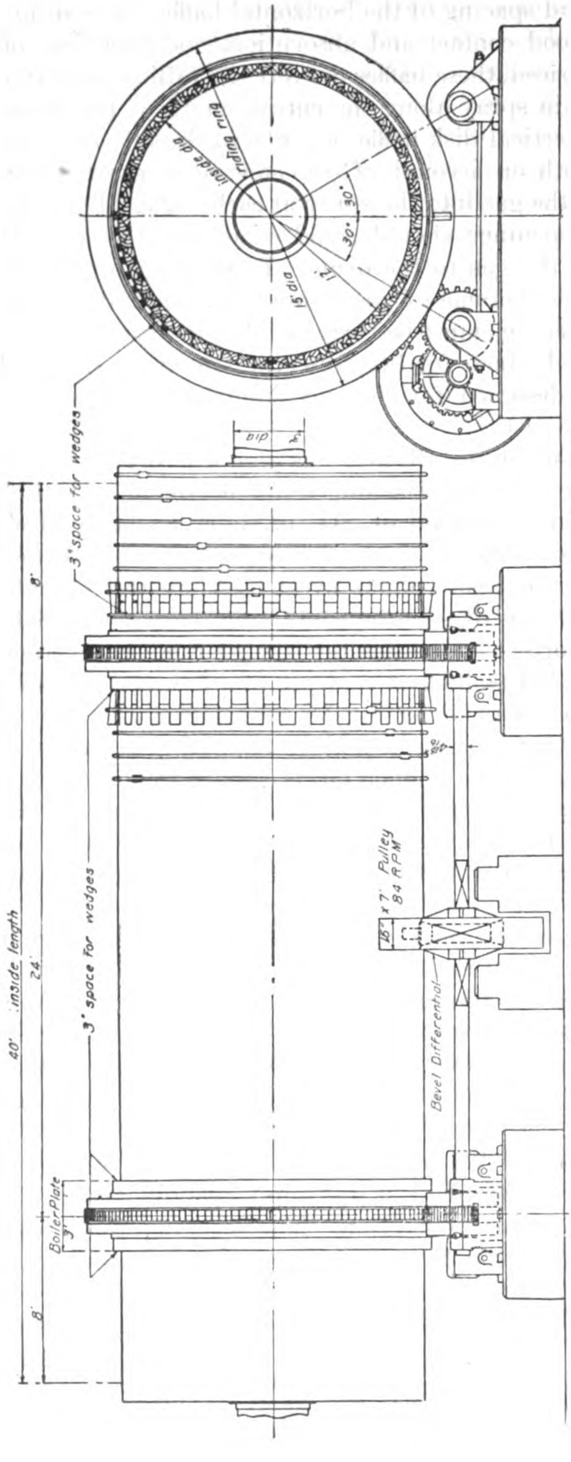

FIGURE 10.—250-ton leaching drum, showing proposed double-gear differentially compensated drive.

This drum satisfactorily handled all the tonnage for which the roasting plant could supply leaching reagent. A maximum capacity of 60 tons per 24-hour day was reached, beyond which the furnace could not supply SO_2. Consequently, the furnace, not the drum, was the limiting factor. Subsequent work at Tucson with the small pilot plant indicates that in all probability economical capacity had been approached in the Clifton drum. It is to be expected that the capacity of a drum of given size will vary for ores of different chemical and physical characteristics. The principal variables are: Acid-consuming constituents; rate of reaction; the best combination of pulp density, gas volume and its SO_2 content.

The design of a 250-ton unit was taken up with J. B.

Cooper, southwestern engineer for the Allis-Chalmers Manufacturing Co., who visited the Miami, Clifton, and Tucson plants. In the specifications submitted to the company a 12 by 30 foot drum was estimated to have a capacity upwards of 250 tons and a 15 by 40 foot drum as having a capacity upwards of 500 tons.

The Allis-Chalmers Manufacturing Co. later submitted a preliminary design, shown in Figure 10, with a drum 40 feet long, or 10 feet longer than necessary. The shell is to be built of 6-inch wooden staves, making its outside diameter 13 feet. The riding rings and gear rings are combined as in large converters. The riding rings will be backed on the inside with three-fourths-inch plate-steel rings about 36 inches wide, which will give good bearing and wedging surface. The turning effort will be applied through both riding rings which are provided with gear teeth in their centers, thus minimizing the transmission of torsion through the shell. This drive will be accommodated by a differential gear mounted at the center of the drive shaft, which will equalize the drive on both ends as closely as possible. The estimated weight of the ironwork is 75,000 pounds, and the estimated price, f. o. b. Milwaukee, is $13,500. The estimated cost of the leaching drum, set up complete with all attachments and connections, but exclusive of auxiliary plant and power consideration, is under $25,000. This estimate contemplates average Arizona conditions and simple foundation requirements. It is estimated that the power requirements of the 250-ton drum and blower will be well under 50 horsepower. The Miami 100-ton SO_2 leaching plant required 20 actual horsepower for operation of leaching drum, suction blower, and roasting furnace.

TABLE 19.—*Drum dimensions affecting capacity.*

Diameter of drum.	Length of drum, feet.	Bucket lifts, in inches.	Number of lifts.	Revolutions per minute.	Calculated capacity, tons per 24-hour day.
Tucson, 4 feet	16	2½	25	16	20
Clifton, 5 feet	20	2¾ net.	30	14	25
Miami, 7 feet 6 inches	40	4¾ net.	47	8	100
New design, 12 feet	30	6¾ net.	75	6	250
New design, 15 feet	40	10½ net.	95	4	500

ANALYTICAL METHODS.

1. DETERMINATION OF NONSULPHIDE COPPER.

Research work on these comparatively low-grade mixed ores was decidedly complicated by the fact that no really dependable method was known for the selective determination of the sulphide copper and of the nonsulphide copper in control samples. When the percentages

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of copper are very small, a variation of 0.05 to 0.10 per cent in an analysis may make considerable difference in judging an operation. The difficulty does not lie in the actual determination of copper, but in the method used to dissolve the nonsulphide copper in the pulp. The sulphuric-acid method of dissolution is commonly used in the laboratories of the large copper companies but with considerable variation of details; the treatment varying all the way from rolling cold with 5 per cent H_2SO_4 for two hours to boiling for three minutes with 10 per cent H_2SO_4. The method is open to the following objections:

Dissolved copper is likely to precipitate on metallic iron (grinding iron) in the sample. This cement copper is practically insoluble in dilute H_2SO_4; therefore, the oxidized copper returns are correspondingly low. Only half the copper present as cuprite is dissolved, the other half is precipitated as metallic copper and is not detected by the assay for oxidized copper. Chalcocite, tenorite, covelite, bornite, and chalcopyrite are all soluble enough in dilute sulphuric acid under oxidizing conditions to affect the determinations; the amount thus dissolved is erroneously reported as oxidized copper. In short, the sulphuric-acid method of dissolution is unreliable as a basis for correct selective determinations. A method of dissolution, known as the sulphur-dioxide method, developed at the Southwest experiment station, avoids the aforementioned difficulties. It has been fully described in Technical Paper 198, and in the technical press.[16] After using the method three years the writers conclude that the result it gives are correct within the limit of experimental error.

Determinations of nonsulphide copper are made at the station either by the iodide method or by the electrolytic method applied to solutions obtained by treating pulps with SO_2 in the following manner:

DISSOLUTION.

Place 2 to 5 grams of pulp, ground to 150 mesh, in a 16-ounce bottle and add 100 c. c. of a 4 per cent solution of SO_2 in distilled water. Cork the bottle tightly to prevent escape of gas and roll for two hours on a bottle-rolling machine. Wash out the bottle onto a fine filter; wash the filter thoroughly with hot water, and retain the filtrate in a 250-c. c. beaker. All the nonsulphide copper is now in solution in the beaker, and the procedure from this point diverges according to the method of determination chosen.

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[16] van Barneveld, Chas. E., and Leaver, E. S., Sulphur dioxide method for determining copper minerals in partly oxidized ores, Met. and Chem. Eng., Feb. 15, 1918, vol. 18, p. 203; Maier, C. G., Sulphur and copper oxide determination, Eng. and Min. Jour., Feb. 23, 1918, vol. 105, p. 372; van Barneveld, Chas. E., and Leaver, E. S., Methods for determining copper minerals in partly oxidized ores, Eng. and Min. Jour., Mar. 23, 1918, vol. 105, p. 552; van Arsdale, G. D., Determining copper minerals in ores, Eng. and Min. Jour., April 6, 1918, vol. 105, p. 645.

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IODIDE METHOD.

Place the beaker containing the filtrate on a hot plate, boil off the excess SO_2. During this boiling the solution turns dark brown and a brownish-black precipitate, probably cupro-cupric sulphite, forms; this redissolves and the solution clears during subsequent boiling with sulphuric acid. When the SO_2 is boiled off remove the beaker from the hot plate and allow it to cool 10 minutes in order that it will not boil over when aluminum is added. When cool add 10 c. c. of 50 per cent sulphuric acid and 1 square inch of sheet aluminum. Place the beaker on the hot plate and boil 20 minutes to precipitate the copper. Remove the beaker, wash the cover and sides with hydrogen-sulphide water; transfer the precipitated copper onto a filter paper and wash with hydrogen-sulphide water to remove all iron. Replace the beaker containing filtrate with a 300-c. c. Erlenmeyer flask. Punch a hole in the filter paper and wash the precipitate into flask. Add 5 c. c. of nitric acid to the original beaker containing the aluminum to dissolve any remaining copper and pour this over the filter paper. Treat the paper with bromine water to insure its being clean and to oxidize any arsenic or antimony that may be present and wash it clean with hot water. Boil the solution in the flask down to about 5 c. c.; cool; add ammonia in slight excess. Boil off excess ammonia, add 3 c. c. acetic acid, and boil one minute. Cool to room temperature, add an excess of potassium iodide, and titrate with standard sodium thiosulphate solution, using starch solution as indicator.

When this method is used regularly in a properly equipped laboratory from 50 to 75 determinations of nonsulphide copper may be made in a shift by one analyst. The necessary equipment includes: A bottle-rolling machine large enough to accommodate at one time half the number of samples to be run in a day; convenient hot-plate arrangement; convenient equipment for filtering and washing; and a regular supply of liquid SO_2 in drums of convenient size.

Generally speaking, the sulphuric-acid method is faster than the SO_2 method, and with it results, such as they are, may be obtained in two hours less time. When single determinations are to be made this may be regarded as a point against the SO_2 method. When batches of 20 or more determinations are handled this objection loses its force. The additional time is consumed by two routine operations, rolling and boiling, that require little manipulation and no supervision; therefore the operator need not lose over 25 per cent of this time. If properly prepared samples from the mill or from experimental work are turned into the laboratory by 3 p. m., results should be available by noon of the day following.

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The method originally adopted at the Southwest station for determining nonsulphide copper was electrolytic determination following SO_2 dissolution. The procedure was slow, as boiling down large volumes of solution was considered necessary, and the method was replaced at the suggestion of W. G. Scott and A. F. Hallett by the iodide method as described above. Later, at the suggestion of L. R. Eckman, the electrolytic method was modified, as described below, and is at present in use.

ELECTROLYTIC METHOD.

To the filtrate in the beaker add 5 c. c. concentrated nitric acid. Cover the beaker with watch glasses and boil for 15 minutes, thereby boiling off or oxidizing most of the SO_2. Remove solutions from the hot plate. oxidize remaining SO_2 by adding 10 c. c. of hydrogen peroxide (ordinary 3 per cent H_2O_2). Cool for five minutes, dilute to 200 c. c., and electrolyze. Complete oxidation is indicated by absence of SO_2 odor and by the solution turning light brown from oxidation of any ferrous iron present. The electrolyte must be free from SO_2 or sulphites; the latter would liberate SO_2 during electrolysis, and the SO_2 would be reduced to H_2S, which would precipitate some of the copper as sulphide, thereby introducing an error. With a 10-unit electrolytic outfit, 20 total copper and 20 nonsulphide copper determinations may readily be made in a seven-hour shift with time available for miscellaneous work while the coppers are electrolyzing. The electrolytic method is recommended for ores known to be free from interfering elements such as arsenic, antimony, and bismuth. Most of the oxidized copper ores of the Southwest are of this class. For impure or unknown ores the iodide method is recommended.

Two corrections to be made in the method described in Technical Paper 198, reproduced in the technical press, are mentioned here. The statement is made that: "Metallic iron in ordinary quantities, even up to 2 per cent, dissolves rapidly and has no effect on the determination, provided there is a strong excess of SO_2, introduced as SO_2 solution." Subsequent work has proved results obtained by this method to be constant and to be substantially correct when metallic iron is present in amounts *under 1* per cent. Investigation of a wide range of mill products obtained under all sorts of crushing conditions and of laboratory pulps prepared in soft-iron disk grinders followed by bucking, disclosed an average metallic content of 0.2 per cent; occasional samples contained as high as 0.5 per cent iron. While it is theoretically possible that part of this iron may, in the presence of SO_2, precipitate Cu as sulphide from sulphate solutions, careful investigation of a large number of assays made under these conditions shows the error introduced from this source to be negligible. With metallic iron in excess of 1 per cent this source of error becomes more important and the results are questionable. The excess of iron should be removed, and it is a simple matter to remove enough iron with a magnet to make the metallic iron content of samples less than 0.5 per cent. As a precaution against errors from this source, it is advisable to investigate the metallic-iron content of new samples. The regular run of samples from a familiar source should be checked periodically.

The other statement, in Technical Paper 198, which must be qualified is to the effect that the sulphide copper minerals are not affected by SO_2. Former work seemed to offer abundant evidence of the correctness of this statement, which is corroborated by standard textbooks[17]. Subsequent investigation disclosed the fact that, using SO_2 in the manner indicated in this analytical method results in a slight dissolution of sulphide copper. The volume of air introduced with the H_2SO_3 is not sufficient to give appreciable oxidizing conditions. The amount of sulphide copper dissolved is so small as to be insignificant. In short, the results obtained are well within the limit of experimental error. This statement should not be considered as having a bearing on leaching conditions in the commercial leaching drum, for there a minimum of 0.5 per cent iron is purposely retained in solution and an abundance of hot air is directed into the drum to furnish an excess of oxygen—conditions that make for the dissolution of copper in sulphide form.

Attention is called to the fact that cuprite is completely soluble in SO_2, whereas in dissolution by sulphuric acid only one-half the copper present as cuprite is dissolved. Metallic copper in the form of scales should be removed from the assay sample in the usual manner. Finely divided (minus 150 mesh) metallic copper, being soluble in SO_2, will be reported as nonsulphide copper.

2. DETERMINATION OF SO_2 IN PURE SO_2 SOLUTION.

Determination of SO_2 in pure SO_2 solution is necessary in connection with the SO_2 method for determining nonsulphide copper, just described. The procedure is as follows:

To 10 c. c. of $N/10$ iodine solution in a beaker or flask add 90 c. c. of water, using starch as an indicator. From a graduated 10 c. c. pipette add SO_2 solution drop by drop until the blue solution becomes colorless. The following equation will then give the value of the SO_2 in solution:

$$\frac{.0032 \times 100 \times 10}{\text{No. c. c. of } SO_2 \text{ solution needed}} = \text{per cent } SO_2 \text{ in solution.}$$

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[17] Greenawalt, Wm. E., Hydrometallurgy of copper, 1912, p. 175.

PLANT CONTROL.

Solutions containing undissociated sulphites, bisulphites, sulphates, H_2SO_3, H_2SO_4 and their resulting ions, including those of ferric and ferrous iron, present a complex and difficult problem. No standard rapid methods, such as are required for ordinary plant control, are available. The methods hereinafter described are presented with full recognition of their limitations; they have little absolute value, yet the relative results they give have, on the whole, proved satisfactory for plant control. The personal equation enters into their use. Familiarity with plant conditions and careful manipulation will do much toward controlling their apparent imperfections.

3. SO_2 AND SULPHITES IN DRUM SOLUTIONS.

To 10 c. c. (or less, depending on the strength of the solution) of *N*/10 iodine solution in a beaker or flask add 80 c. c. water, starch solution and 10 c. c. HCl. From a graduated 10 c. c. pipette add drum solution drop by drop until the solution is decolorized:

$$\frac{0.0032\times100\times10}{\text{No. c. c. of } SO_2 \text{ solution needed}} = \text{per cent } SO_2 \text{ in solution.}$$

This method is identical with analytical method 2, but when applied to drum solutions is subject to various conditions that do not obtain in the analytical procedure. It actually reports total sulphites including free SO_2; the results therefore are "high." Any ferric iron in solution will liberate iodine from the KI present in the standard solution and would tend toward "low" results. However, the quantity of ferric salts ordinarily present would be small and errors from this source would be negligible. In short, this is a comparative method, to be used on drum solutions for plant control only.

4. SULPHURIC ACID CONTENT OF DRUM SOLUTION.

Applied to a mixture containing hydrogen ions, metallic ions, sulphite and sulphate ions, in a condition of complex and unknown equilibrium, the term "sulphuric acid content" is rather indefinite. There is no convenient analytical method that gives the actual equilibrium concentration of any of the constituents; in all proposed methods the final value obtained is affected by the shift in equilibrium which takes place during analysis. The choice of an analytical method is somewhat arbitrary, the "sulphuric acid concentration" being, in fact, an arbitrary term representing the concentration indicated by the particular analytical method chosen. In titrating drum solutions directly with standard NaOH or Na_2CO_3, any easily hydrolyzed salts of iron or aluminum present cause semicolloidal, brownish precipitates to form before the hydrogen ion concentration is reduced to a point where the common indicators change color, thus obstructing the end point of the titration. This is largely overcome by a method described by Rankin.[18] Following is a slight modification of this method, as used at the Tucson laboratory:

Pipette 5 or 10 c. c. of the acid solution into a beaker, boil on hot plate until free from dissolved SO_2, add 2 c. c. of 50 per cent KI solution. This reduces the ferric iron present to the ferrous state, according to the following reaction:

$$Fe_2(SO_4)_3+2KI=K_2SO_4+2FeSO_4+I_2.$$

Add enough sodium thiosulphate to decolorize the free iodine liberated by the ferric iron. Filter off the resulting white precipitate of cuprous iodide and wash with hot water. Dilute the clear colorless filtrate with distilled water; add a few drops of methyl orange and titrate the solution with $N/10$ Na_2CO_3 solution to a yellow color:

$$\frac{\text{No. c. c. } Na_2CO_3\times 0.0049\times 100}{\text{No. c. c. solution taken}}=\text{Per cent } H_2SO_4.$$

Attention is called to the fact that during the boiling, a shift in the equilibrium occurs. A definite concentration of acid will, however, be determined in the boiled solution; a comparison of the values so obtained will give satisfactory data for purposes of plant control.

5. TOTAL ACIDITY.

The results obtained from determination 3, calculated in terms of H_2SO_4, added to those obtained from determination 4, will give a close approximation of total acidity. This may be expressed as a percentage or in terms normal with reference to the drum solution. To illustrate the latter method: If 10 c. c. of drum solution required 10 c. c. of $N/10$ Na_2CO_3 to exactly neutralize the total acid, the acidity of the drum solutions would be exactly 1/10 normal; if 20 c. c. of $N/10$ Na_2CO_3 were required, the acidity would be exactly 1/5 normal. Since method 3 estimates total sulphites and method 4 estimates sulphuric acid, less any sulphites present to react with it, the sum of the results from 3 and 4 will be "high" only when the total metallic sulphites present exceed the amount which the sulphuric acid present can decompose. In any case, the true value for total acidity would be obtained by boiling the solution, absorbing any expelled SO_2 in standard iodine solution, and estimating the H_2SO_4 in the residual solution. This method was used in comparison with method above described, and the results were found to be in close agreement.

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[18] Met. and Chem. Eng., Jan. 15, 1918, vol. 18, p. 96; Rankin, James J., Acidity determination in water, leach liquors, mine waters, etc.

6. SO_2 IN FURNACE GAS.

Place 10 to 50 c. c. of $N/10$ iodine solution and starch indicator in a small flask filled with broken glass tubing or beads. Aspirate a quantity of the gas to be tested through this iodine solution until it is discolored. The water from the aspirator bottle is caught in a graduated flask. The indicated volume of water corresponds to the volume of gas minus the volume of SO_2 which passed through the iodine solution. For convenience, the iodine is standardized by volume, the value of $N/10$ iodine is given in terms of c. c. of SO_2 per c. c. of iodine. The per cent SO_2 is then calculated as follows:

$$\frac{\text{No. c. c. iodine} \times \text{its } SO_2 \text{ value in c. c.} \times 100}{\text{Volume } H_2O + \text{volume} SO_2} = \text{per cent } SO_2 \text{ (by volume) in gas.}$$

7. ACID REQUIREMENT OF ORES.

Different research laboratories have different methods for determining the probable acid requirements of an ore. At best the determination is only approximate. The method used at the Tucson laboratory is as follows: Place 1 gram of pulp in a beaker, add 5 c. c. of 5 per cent H_2SO_4 solution, bring to a boil and let stand for one hour. Add 2 c. c. of 50 per cent KI, add a few c. c. of sodium thiosulphate to destroy liberated iodine. Filter off the pulp and precipitated cuprous iodide, dilute filtrate to 150 c. c. with distilled water, titrate with $N/10$ Na_2CO_3. Make a similar titration of 5 c. c. of the 5 per cent H_2SO_4 solution used. The difference in the titrations represents the acid consumed:

1 c. c. $N/10$ $Na_2CO_3 = 0.0049$ gram H_2SO_4.
$0.0049\ (T_1 - T_2) =$ grams H_2SO_4 consumed by 1 gram of ore.
$0.0049\ (T_1 - T_2) \times 100 = H_2SO_4$ consumed (in per cent decimals).
H_2SO_4 (per cent decimals) $\times 2000 =$ pounds H_2SO_4 per ton.
H_2SO_4 (per cent decimals) $\times 652 =$ pounds S. per ton.

Upon request, the Pacific experiment station, Berkeley, Calif, detailed L. E. Roberts, physical chemist, to investigate analytical and plant-control methods. His conclusions are presented in the following summary abstracted from his report:

> The methods of analysis described above have been examined and seem accurate within the limitations stated in the text. Considerable experimental work was done on plant control, methods 3, 4, and 5, with a view to determining the magnitude of the errors involved. The difficulty in analyzing a mixture as complex as these drum solutions is inherent in the fact that the ordinary analytical methods ignore the changes in equilibrium which take place during the analysis and give final values instead of initial equilibrium values. Corrections could be applied which would give the initial values, if it were possible to determine the equilibrium concentration of each constituent independently, using drum solutions. This has not been possible, but the methods given have been compared with other methods which would have different sources of error. Thus, SO_2 and sulphites were determined successively by method 3 by dis-

tilling a sample of solution with standard iodine in a Bunsen chlorine-absorption bulb, by aeration of solution, passing the gas through standard iodine. Substantial agreement was obtained in each case. Total acid was determined by adding the sulphuric-acid content obtained by method 4 to the values for sulphite as determined above, and, of course, agreement was found. The values for total acid as found by successively titrating with standard iodine, reducing the ferric iron with KI, decolorizing by thiosulphate and titrating with Na_2CO_3, were slightly higher, as might be expected from the formation of hydriodic acid in the oxidation of SO_2 by iodine.

The agreement obtained from these comparisons warrants the conclusion that the errors in any case are very small and that the methods may be safely used for purposes of plant control.

LIST OF PUBLICATIONS ON TREATMENT OF COPPER ORES.

A limited supply of the following publications of the Bureau of Mines has been printed and is available for free distribution until the edition is exhausted. Requests for all publications can not be granted, and to insure equitable distribution applicants are requested to limit their selection to publications that may be of especial interest to them. Requests for publications should be addressed to the Director of Mines.

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PUBLICATIONS AVAILABLE FOR FREE DISTRIBUTION.

BULLETIN 205. Flotation tests of Idaho ores, by C. A. Wright, J. G. Parmelee, and J. T. Norton. 1921. 67 pp., 8 pls., 1 fig.

TECHNICAL PAPER 86. Ore-sampling conditions in the West, by T. R. Woodbridge. 1916. 96 pp., 5 pls., 17 figs.

TECHNICAL PAPER 182. Flotation of chalcopyrite in chalcopyrite-pyrrhotite ores of southern Oregon, by W. H. Coghill. 1918. 13 pp., 1 fig.

PUBLICATIONS THAT MAY BE OBTAINED ONLY THROUGH THE SUPERINTENDENT OF DOCUMENTS.

BULLETIN 81. The smelting of copper ores in the electric furnace, by D. A. Lyon and R. M. Kenney. 1915. 80 pp., 6 figs. 10 cents.

BULLETIN 107. Prospecting and mining of copper ore at Santa Rita, N. Mex. by D. F. MacDonald and Charles Enzian. 1916. 122 pp., 10 pls., 20 figs. 25 cents.

BULLETIN 122. The principles and practice of sampling metallurgical materials, with special reference to the sampling of copper bullion, by Edward Keller. 1916. 102 pp., 13 pls., 31 figs. 20 cents.

TECHNICAL PAPER 143. The ores of copper, lead, gold, and silver, by H. C. Fulton. 1916. 41 pp. 5 cents.

TECHNICAL PAPER 198. Sulphur dioxide method for determining copper minerals in partly oxidized ores, by C. E. van Barneveld and E. S. Leaver. 1918. 14 pp., 1 fig. 5 cents.

APPENDIX.

EXPERIMENTS DURING 1922 ON THE FLOTATION OF CEMENT COPPER.

Walter G. Scott, of the research staff of the Inspiration Copper Co., was temporarily associated with the Southwest station as assistant metallurgist while operations at Inspiration were suspended. When operations were resumed he returned to Inspiration, but was retained by the Bureau of Mines as consulting metallurgist to permit him to carry out some experiments in connection with the flotation of cement copper. An abstract of a report by Mr. Scott on these experiments is printed below.

ABSTRACT OF REPORT BY WALTER G. SCOTT.

The flotation of cement copper obtained by leaching nonsulphide copper with sulphurous or sulphuric acid and precipitation of the dissolved copper on sponge iron has been tried with varied or erratic success; the problem is to obtain good results continuously. The successful flotation of cement copper in a particular laboratory often is not duplicated when attempted under other laboratory conditions, even by the same operator. Generally, a flotation problem includes conditions that call for a special study of each ore, as is evidenced by the fact that each mill follows a procedure peculiar to that ore alone. An ore amenable to flotation to-day, if permitted to remain in open storage any length of time, will give entirely different results under seemingly identical operating conditions.

Results obtained with fresh water will differ considerably from those obtained with reclaimed water. Again, a flotation problem may be solved with city water, but the water available at the property may give entirely different results. It is not practicable to prepare synthetically a water that will give results parallel with those obtained with the natural camp or mill water used in making the original tests.

To make for a uniform procedure, the flow sheet below was followed:

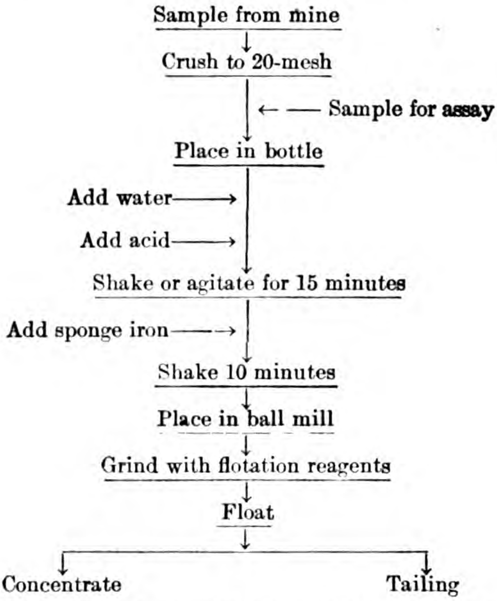

FIGURE 11.—Flow sheet used in flotation tests of cement copper.

Comparison of the average results obtained with various oils indicates that successful flotation of cement copper does not depend on the use of a particular oil but does depend on pulp conditions.

In order to cover systematically the range between the acid and the alkaline field, several series of tests were made in which the standard mixture of coal tar and pine oil was used and different quantities of lime (1 to 20 pounds per ton of ore) were added in each test. The best result were obtained from a practically neutral pulp.

TABLE 20.—*Effect of lime on flotation.*

CaO added per ton of ore, pounds.	Feed.		Concentrate, total copper, per cent.	Tailing, total copper, per cent.	**Remarks.**
	Total copper, per cent.	Sulphide copper, per cent.			
8	1.70	0.64	10.40	0.45	Slightly acid.
9	1.70	.64	10.40	.31	
10	1.70	.64	10.40	.26	
11	1.79	.64	11.66	.24	
12	1.70	.64	11.16	.16	Neutral.
13	1.70	.64	10.84	.20	
14	1.70	.64	10.84	.34	
15	1.70	.64	12.20	.45	
16	1.70	.64	12.20	.47	Alkaline.

Tests under conditions that gave the best results as indicated above were repeatedly checked, and a total recovery of over 90 per cent was obtained.

It was thought that assaying the pulp solution for SO_4 would indicate the amount of lime necessary to satisfy this radical, and that a slight excess would make for best results. The action of lime (CaO) was found to be slow, requiring excessive time for complete action; while an uncompleted action upset the desired flotation balance. The use of limestone in lump form seems practicable, as the excess is easily controlled.

It is noticeable that a thin pulp (4:1 or, better, 6:1) gives better extraction and a cleaner, higher grade concentrate than is obtainable with a thick pulp, such as 2:1.

RESULTS AT TUCSON LABORATORY.

Work at the Tucson laboratory during 1922 indicates that the addition of CaO or of limestone is unnecessary; just as good results are obtained without it. When the degree of acidity of the pulp is slight, the addition of sponge iron will produce neutral pulp conditions. The fact is that the real problem seems to be the physical condition of the pulp rather than its degree of acidity or alkalinity.

The relative efficiencies of the violent agitation type and the pneumatic type of flotation machines for the recovery of cement copper have been in controversy. Although the general opinion seems to be that the violent agitation type produces conditions within the cell which should make for the highest recovery, yet experience at Tucson indicates that with certain preliminary precautions the pneumatic cell gives just as good results. These precautions include: (*a*) The emulsifying and spatial distribution of oil; (*b*) finely divided cement copper. When fairly coarse sponge iron was used, the precipitated copper held together in rounded globules that did not float in the pneumatic cell; but the violent agitation type of flotation cell disintegrates these globules so much that good flotation is obtainable. On the other hand, if the pulp containing the globules that do not float in the pneumatic cell is first passed through a ball mill to break up the cement globules, then the copper will float just as well in the pneumatic cell.

Under the flow sheet below, which was developed by R. V. Thurston, associate metallurgist at the Southwest experiment station, the authors have obtained *in one operation* uniformly high flotation recovery (about 90 per cent) of the total copper in the pulp—that is, of the precipitated cement copper and of the sulphide copper originally present in the mixed ore.

Flow sheet, mechanical agitation machine.

750 grams of ore crushed to 35 mesh.

750 c. c. acid solution: either 2 per cent H_2SO_4 or ferric sulphate solution 1 per cent Fe^{+++}, 2 per cent H_2SO_4.

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Leach for 30 minutes with frequent agitation.

Add a small quantity of sponge iron, not quite enough for complete precipitation of Cu.

Frequent agitation for 10 minutes.

Add enough sponge iron to complete precipitation of Cu.

Place pulp in flotation machine, oil, float 15 to 20 minutes.

Flow sheet, pneumatic type machine.

1,000 grams of ore crushed to 35 mesh.

1,000 c. c. acid solution: either 2 per cent H_2SO_4 or ferric sulphate 1 per cent Fe^{+++}, 2 per cent H_2SO_4.

Leach for 30 minutes with frequent agitation.

Add sponge iron as above.

Oil the pulp and grind in ball mill for 30 minutes with either iron balls or pebbles (better grinding with iron balls).

Float 15 to 20 minutes.

TABLE 21.—*Comparative results with Walker River ore.*

Mechanical agitation machine.				Pneumatic type machine.			
Copper content of feed: Total Cu, 2.70 per cent; nonsulphide Cu, 2.60 per cent.				Copper content of feed: Total Cu, 2.70 per cent; nonsulphide Cu, 2.60 per cent.			
Flotation results.				Flotation results.			
Cu, per cent.		Apparent recovery, per cent.	Remarks.	Cu, per cent.		Apparent recovery, per cent.	Remarks.
Tailing.	Concentrate.			Tailing.	Concentrate.		
0.24	13.08	88.2	Sulphuric acid leach.	0.25	5.98	93.7	Sulphuric acid leach.
.34	14.22	87.9	Do.	.35	6.94	89.3	Do.
.33	11.06	88.8	Ferric sulphate acid leach.	.19	6.34	91.0	Ferric sulphate acid leach.
.27	15.32	89.2	Do.	.19	9.00	92.7	Do.

TABLE 22.—*Comparative results with Miami complex ore.*

Mechanical agitation machine.				Pneumatic type machine.			
Copper content of feed: Total Cu, 2.31 per cent; nonsulphide Cu, 0.73 per cent.				Copper content of feed: Total Cu, 2.31 per cent; nonsulphide Cu, 0.73 per cent.			
Flotation results.				Flotation results.			
Cu, per cent.		Apparent recovery, per cent.	Remarks.	Cu, per cent.		Apparent recovery, per cent.	Remarks.
Tailing.	Concentrate.			Tailing.	Concentrate.		
0.21	31.67	91.8	Sulphuric acid leach.	0.23	19.96	91.3	Sulphuric acid leach.
.28	24.44	89.0	Do.	.22	20.54	91.6	Do.
.24	21.90	90.5	Do.	.21	18.92	92.0	Do.
.15	16.74	94.5	Ferric sulphate acid leach.	.23	17.88	91.2	Ferric sulphate acid leach.
.18	18.50	93.0	Do.	.25	26.94	90.0	Do.
.21	19.94	91.7	Do.	.27	18.84	89.7	Do.

The Chino Copper Co., Hurley, N. Mex., is now commercially floating cement copper at its 200-ton experimental plant. This plant receives a part of the regular waste tailing from the main concentrator; only enough sulphuric acid is added to account for the easily soluble constituents. Pulp containing both sand and slime flows continuously through agitation tanks; one-half hour is allowed for acid contact. Sponge iron is added in the proportion of about 1.2 iron to 1 of dissolved copper. Continuous flow through small precipitation tanks allows 15 minutes for completing precipitation. A reconstructed oil containing 5 per cent sulphur is the flotation agent. The new Janney flotation machine, a combination of the violent agitation and pneumatic cell types, is used. The feed entering the leaching plant contains less than 0.5 per cent total copper; the tailing contains approximately 0.15 per cent total copper. These values represent the combined sulphide and nonsulphide copper. The percentage of recovery of cement copper is probably 80 per cent—a very good figure in view of the low grade of this complex concentrator tailing. The grade of concentrates is quite satisfactory and compares favorably with the general mill concentrate.

Where the nonsulphide copper content of an ore is under 1 per cent, precipitation in the pulp with recovery of the cement copper by flotation will probably find favor in commercial operations. On the other hand, the higher grade leaching ores, containing 2 per cent or more of soluble copper, may give better results by precipitation from clear solution.

The future of copper leaching followed by flotation recovery depends largely on the manufacture of sponge iron. At Hurley the Chino Copper Co. is successfully running a 6-ton furnace that deoxidizes magnetite obtained as a by-product from the general milling operation. This furnace has a single hearth, 12 feet in diameter, inclosed with fire brick in beehive form. Heat is generated by an oil flame which passes through carborundum tubes situated in the upper part of the beehive. The radiation from the tubes maintains a temperature of 950° C. at the hearth. The charge, consisting of magnetite plus 40 per cent (by weight) of bituminous coal or of carbo-coal (a partly coked bituminous coal), is fed at the center of the revolving hearth, and is discharged at the circumference, where it drops to a water-cooled worm conveyor, then passes to a magnetic separator. The sponge iron made is remarkably uniform in grade and bears no evidence of fusion or sintering. The present cost is estimated at $18 per ton; this may be cut to nearly $12 in large-scale work.

The Tintic Milling Co., Silver City, Utah, has in operation a 3-ton furnace developed by the Northwest experiment station of the

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Bureau of Mines. This furnace is a continuously operated, internally fired, rotary kiln, which consists of a tube 22 feet long by 44 inches in diameter, used as a preheater, and an enlarged section 5 feet long by 60 inches in diameter for completing the deoxidation. A charge—equal weights of hematite ore and bituminous coal—passes the 22-foot section in 11 minutes and remains in the enlarged section about an hour, discharging through a Thermalloy pipe set obliquely through the end wall of the enlarged section. The proper temperature, 950° C., is obtained by a coal or oil flame entering at the enlarged end. This simple sponge-iron furnace has excellent possibilities where the price of coal is relatively low.

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